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Division of Chemical Science

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(OTDELENIE KHIMICHESKIKH NAUK)

IN ENGLISH TRANSLATION

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BULLETIN OF THE ACADEMY OF SCIENCES OF THE USSR

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1960, Number 4 April

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On pages 1-3 of this issue of the Russian text there appears an article commemorating the ninetieth anniversary of the birth of V.I. Lenin. Since the article does not deal with either details of chemical research or even its historical development, it has been omitted from the translation.

ERRATA

No. 12, 1959

The following formula should appear in the Bulletin of the Academy of Sciences USSR, Division of Chemical Science on page 2025, replacing the formula published.

$$X(CH_2)_nCH{=}CCl_2 + Cl_2 \xrightarrow{HCOOH} [X(CH_2)_nCHClCCl_2OCOH] \xrightarrow{H_2O} X(CH_2)_nCHClCOOH.$$

INVESTIGATION OF THE SYSTEM $Ti(SO_4)_2 - H_2SO_4 - NaOH - H_2O$ (20 and 25°) BY METHODS OF SOLUBILITY AND APPARENT VOLUME OF PRECIPITATE

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The purpose of the present work was to accelerate the study of chemical systems by the simultaneous use of two methods (solubility and measurement of the apparent volume of the precipitate), but with the use of only one vessel and to determine the mechanism of the precipitation of tetravalent titanium with alkali from sulfuric acid solution*. Despite the theoretical and practical interest in the elucidation of the mechanism of precipitation, there has been no work in this direction as yet. There is wide use in chemical technology and analysis of processes based on the precipitation from solutions of slightly soluble basic salts, bases, acid salts, and acids. The control of these processes and the development of new precipitation conditions require a knowledge of the mechanism of the precipitation of these compounds. The choice of a system with $Ti(SO_4)_2$ for study was not by chance, for the latter is one of the most important salts of titanium as the preparation of titanium compounds normally proceeds through the formation of the sulfate.

EXPERIMENTAL

Into a 100-ml measuring cylinder or another measuring vessel (Fig. 1) with 0.1 ml divisions were introduced calculated volumes of the following solutions: 1) a constant volume of $Ti(SO_4)_2$ solution (10 ml, 0.125 M), containing sufficient sulfuric acid to prevent hydrolysis (0.155 ml and 0.259 M); 2) carbonate-free NaOH solution in an amount sufficient to neutralize the excess free H_2SO_4 and also excesses corresponding to NaOH : $Ti(SO_4)_2$ ratios from 0 to 5**. The solution was diluted to 100 ml with water and the system stirred with an electric motor in a thermostat (25°) for 24 hr. The stirrer was then stopped, the cylinder closed with a rubber bung, and the contents of the cylinder were shaken several times and allowed to settle in the same thermostat (25°). After 2 or 3 hr the volume of precipitate was measured. The precipitate was removed by filtration through "white strip" filter, the reaction of the filtrate (supernatant solution) determined with an indicator (Methyl orange, Neutral red, and phenolphthalein), and the filtrate also tested for titanium with hydrogen peroxide. Two 40 ml portions of the supernatant solution were then analyzed and the composition of the precipitate calculated from the difference between the amount of ions (Ti^{4+}, SO_4^{2-}, Na^+, OH^-, and H^+) taken and those remaining in the solution. In the case of an acid filtrate, one portion of it was used to determine three or two ions (H^+, Ti^{4+}, and SO_4^{2-}, or H^+ and SO_4^{2-}), depending on whether titanium was present or not. The hydrogen ion content was

*Salts of Ti^{4+} do not exist in aqueous solutions without excess free acid and are hydrolyzed on dilution to form insoluble precipitates.

**The ratio of NaOH : $Ti(SO_4)_2$ in the original mixture will subsequently be denoted by n.

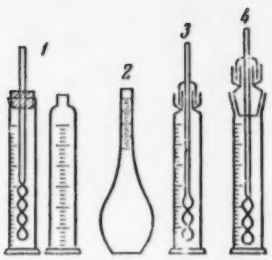

Fig. 1. Vessels for the simultaneous study of systems by the methods of solubility and measurement of the apparent volume of the precipitate: 1) measuring cylinders; 2) flask (for measuring the precipitate volume, it is closed with a rubber bung to the zero division and inverted); 3) measuring cylinder with a liquid seal; 4) measuring cylinder with a demountable liquid seal on a ground-glass joint.

determined by titration with 0.125 M NaOH solution with Methyl orange as indicator. In addition, the hydrogen ion content was also calculated from the difference: $(H_2SO_4 + Na_2SO_4) - Na_2SO_4$. The Ti^{4+} ions were then determined in the same beaker by precipitation of the hydroxide with ammonia, collection of the precipitate, and firing it to TiO_2. The filtrate was acidified with hydrochloric acid and the SO_4^{2-} ions determined by precipitation as $BaSO_4$ with barium chloride. When titanium was absent, the concentration of H^+ ions was determined, the solution acidified with hydrochloric acid, and the SO_4^{2-} ions determined.

In the second portion of the acid filtrate containing titanium, the titanium was separated with ammonia and then determined (parallel determination), the filtrate carefully evaporated in a quartz vessel and fired at 500°, and the residue weighed for the determination of sodium as Na_2SO_4. If the acid filtrate did not contain titanium, the sodium was determined analogously after the filtrate had been made alkaline with ammonia to avoid the formation of $NaHSO_4$. The $(NH_4)_2SO_4$ present voltalized above 350°.

When the filtrate was alkaline, i.e., when titanium was absent from the supernatant solution, the first portion was used to determine the OH^- ion content by titration with 0.1 N H_2SO_4 with Methyl orange as indicator and then, after the solution had been made alkaline with ammonia until it smelled of ammonia or gave a color with phenolphthalein, the sodium was determined by the method described. In this case the second portion was acidified with hydrochloric acid and the SO_4^{2-} ions determined as described above.

We should note that the liquid phase (filtrate), which contained titanium over the range of values of n from 0 to 3, remained clear after being stirred at 25° for a day and standing for a longer period. If the system was stirred for a shorter time and then allowed to stand for ~8 hr, it was possible to isolate from the solution a small amount of precipitate, which was also observed when the apparent volume of the precipitate was measured by Tananaev's procedure (see below). Thus, though there was subsequent polymerization or hydrolysis of $Ti(SO_4)_2$ in the supernatant solution at 25°, it was very slow as complete precipitation of the titanium from the solution was attained only at 100°. On this basis, the data obtained may be considered as corresponding practically to the equilibrium state of the system.

Reaction in the system $Ti(SO_4)_2 - H_2SO_4 - NaOH - H_2O$, studied by means of solubility at 25°. The results obtained are presented in Fig. 2; from them it follows that the precipitation of titanium from dilute sulfuric acid solution began even without the addition of alkali. As the amount of alkali in the starting mixture increased, the amount and volume of the precipitate increased and at n = 3.2 with 0.0125 M $Ti(SO_4)_2$ and 0.0155 M H_2SO_4 in the starting mixture and also at n = 3.2 with the same amount of $Ti(SO_4)_2$, but with the H_2SO_4 concentration increased to 0.0259 M*, titanium could not be detected in the solution with hydrogen peroxide. Thus, even before the addition of an amount of alkali corresponding to the formation of $Ti(OH)_4$ (more accurately, H_2TiO_3; n = 4), the whole of the titanium was in the precipitate. The precipitate also contained H_2SO_4 and with a constant $Ti(SO_4)_2$ content in the system, the ratio of SO_4^{2-} : Ti^{4+} in the precipitate was 0.15 on the average over the range n = 0.0-3.2 with an H_2SO_4 concentration of 0.0155 M and 0.25 over the range n = 0.0-3.3 with an H_2SO_4 concentration of 0.0259 M, i.e., the SO_4^{2-} content of the precipitate increased correspondingly with an increase in the H_2SO_4 content of the system. With a further increase in the alkali content of the solution, i.e., n > 3.3, there was gradual, easy, and complete removal of the SO_4^{2-} ions from the precipitate into the solution (reaction in the solid phase) and at n = 4, the precipitate formed did not contain SO_4^{2-} ions, i.e., it was pure H_2TiO_3, and the reaction solution became neutral. With an increase in n from 4 to 5, excess alkali began to appear in the supernatant solution and there was gradual coprecipitation of NaOH with the precipitate, which did not contain SO_4^{2-} ions and solution of it in alkali did not occur. Over the whole range of values of n studied, i.e., from 0 to 5, the

*In this case, the ordinate at n = 3.3 in Fig. 2 would have corresponded to a precipitate with the composition $H_2TiO_3 \cdot 0.25H_2SO_4$.

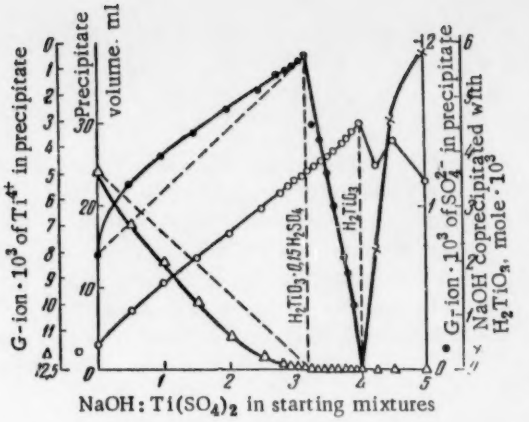
G-ion · 10³ of Ti⁴⁺ in precipitate
Precipitate volume, ml
H₂TiO₃·0.15H₂SO₄
H₂TiO₃
G-ion · 10³ of SO₄²⁻ in precipitate
NaOH coprecipitated with H₂TiO₃, mole · 10³
NaOH : Ti(SO₄)₂ in starting mixtures

Fig. 2. Solubility and apparent volume of precipitate in the system $Ti(SO_4)_2-H_2SO_4-NaOH-H_2O$ (25°).

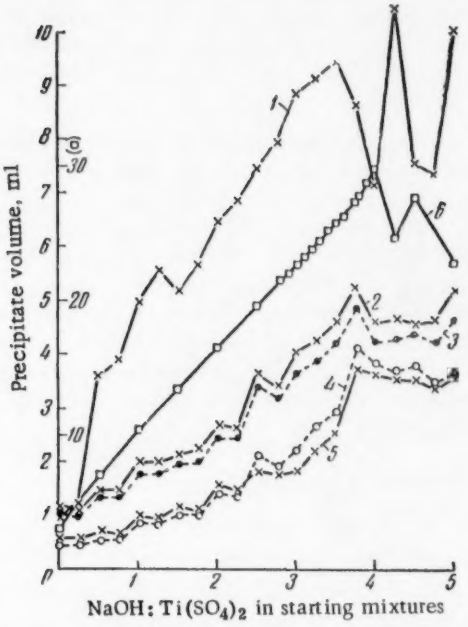

Fig. 3. Change in precipitate volume in the system $Ti(SO_4)_2-H_2SO_4-NaOH-H_2O$ (20°) after: 1—1/4 hr; 2) 2 hr; 3) 3 hr; 4) 24 hr; 5) 48 hr; 6) in a study of solubility(2 hr after settling at 25°).

precipitates did not include Na_2SO_4, which was present in the system. We should note that over the range n = = 0-4 (excluding 4) the ratio of OH^- : Ti^{4+} in the precipitate was less than required for the formation of a precipitate with the formula $Ti(OH)_4$, while over the range n = 0.00-0.75 (1.00), it was less than that required for the formation of a precipitate with the formula TiO $(OH)_2$ (more accurately, H_2TiO_3), even allowing for the SO_4^{2-} ions in the precipitate. The amount of H^+ and OH^- ions required for the formation of these compounds was obtained from water due to hydrolysis of $Ti(SO_4)_2$. The ratio of H^+ : Ti^{4+} in the precipitate actually corresponded to the amount of SO_4^{2-} ions in the precipitate over the whole of the range n = 0-4. No peptization of the precipitate was observed in the system studied at any of the values of n. With complete precipitation of the titanium, i.e., over the range n > 3.3 (3.4)-5.0, the precipitates were no less dense in appearance than over the range n = 0.0-3.3 (3.4). Since the precipitation of titanium is not expressed by a straight line (see Fig. 2), it follows that the composition of the precipitates over the range n = 0.0-3.2 (3.3) is not constant, but changes somewhat with a change in the composition of the starting solution. However, on the basis of the data obtained, it may be assumed, nonetheless, that the main (average) compositions of the precipitates may be represented as $H_2TiO_3 \cdot 0.15\ H_2SO_4$ and $H_2TiO_3 \cdot 0.25\ H_2SO_4$. This is also indicated by the corresponding curves of the SO_4^{2-} content of the precipitate in relation to n (curves with black points in Fig. 2). The highest SO_4^{2-} content of the precipitates corresponds to a value of n of 3.2 and 3.3. Attention is also attracted by the different course of the changes in the SO_4^{2-} concentration in the precipitate on the left and right of these points. On the left, where the solution contains unprecipitated titanium ions, the curve examined has a slope greater than the theoretical slope of H_2SO_4 coprecipiation lines (broken lines in Fig. 2) and this corresponds to an increase on the titanium precipitation curve. On the right side of these points, in those sections from n = 3.3 (3.4) to 4.0, there is a sharp fall in the SO_4^{2-} ion content of the precipitate, which indicates that these ions are readily displaced from the precipitate by OH^- ions.

Investigation of the system $Ti(SO_4)_2-H_2SO_4-NaOH-H_2O$ by measurement of the apparent volume of the precipitate. To a constant amount of 0.0125 M $Ti(SO_4)_2$ solution (with an excess of H_2SO_4 = 0.0155 M) we added water and then NaOH solution [in an amount sufficient to neutralize the excess H_2SO_4 and to create a NaOH : $Ti(SO_4)_2$ ratio from 0 to 5], according to Tananaev's method [1]. The contents (20 ml) of the measuring tubes were mixed manually for 20 min by inversion of the tubes and then the tubes were placed vertically in a stand for the precipitate to settle naturally. The volumes of the precipitates formed (in ml) were read off at regular intervals. Figure 3 shows the kinetics of titanium precipitation by alkali. The white, flocculent precipitate settled and consolidated simultaneously with time, while its apparent volume (density) remained practically unchanged after the second day. Titanium was found in the liquid phase over the range N = 0-3. The precipitates

first formed were soluble in dilute acids, but after 8-hours aging, both the primary precipitates and traces of additional precipitates formed in the range n = 0-3 changed to an insoluble form. The further hydrolysis of $Ti(SO_4)_2$ in the range n = 0-3 after 8-hours aging was apparently due to the system changing from a metastable to a relatively stable and equilibrium state.

Despite further mixing, the precipitate volumes had not changed substantially 24 hr and even 26 days later. The precipitate volume increased with an increase in n from 0 to 4 and reached a maximum at a value of n close to 4, i.e., as might be expected from the equation for complete precipitation of titanium by alkali. Actually, as the solubility data show, there was complete precipitation of titanium much sooner; namely, when n = 3.2 or 3.3 (depending on the excess H_2SO_4 content of the solution), in the form of $H_2TiO_3 \cdot 0.15\ H_2SO_4$ or $H_2TiO_3 \cdot 0.25\ H_2SO_4$, though this does not appear on the curve of precipitate volumes. We should note that an increase in the amount of Na_2SO_4 in the system, formed as a result of alkali neutralization of the excess H_2SO_4 (required to prevent hydrolysis of the $Ti(SO_4)_2$ in the starting solution), did not change the position of the maximum of the precipitate volume in the system.

When n = 4.25, the precipitate volume curves show a minimum (which apparently corresponds to the greatest coagulating effect of OH^- ions), but the precipitate volume corresponding to this minimum is, however, greater than that formed at n = 3.25, when all the titanium is also in the precipitate. When n = 4.5, a second maximum of precipitate volume was observed and this corresponds to a composition of $H_2TiO_3 \cdot 0.35$ NaOH. With a further increase in n to 5, there was a second decrease in the precipitate volume, connected with the coprecipitation of NaOH with the H_2TiO_3 precipitate. When the $Ti(SO_4)_2$ content of the system was increased by a factor of 1.6 and that of H_2SO_4 by 2.6, the picture of titanium precipitation did not change in general, as compared with the initial data, although the SO_4^{2-} content of the precipitate increased (over the range n = 0-4).

A comparison of Figs. 2 and 3 indicates that in the system investigated both by Tananev's procedure (20°) [1] and the procedure proposed by us (25°), despite the difference in temperature, there is a monotonic increase in the precipitate volume as the solution is neutralized with alkali, a maximum in the precipitate volume at n = 3.75-4.00 and in the alkaline region, a minimum at n = 4.25 and a maximum at n = 4.50. In contrast to the precipitate volume curve obtained by our procedure, with some of those obtained by Tananaev's method, the point corresponding to the maximum at n = 3.75 moved with time to n = 4. This was probably due to the establishment of a practically stable equilibrium. In this case, the unstable precipitates $H_2TiO_3 \cdot \chi\ H_2SO_4$, formed initially, gradually lost H_2SO_4 and were converted to pure H_2TiO_3 at n = 4. As the solubility method showed, the extrema on the precipitate volume curves (with the exception of that at n = 4) do not correspond to any chemical compounds and were of a random nature in the investigation by Tananaev's method and they were explained by the nonequilibrium state of the system.

DISCUSSION OF EXPERIMENTAL RESULTS

There are several points of view regarding the state of titanium in sulfuric acid solutions. Some authors consider that titanium is present in the form of the metastable hydrate $TiO_2 \cdot H_2O$, others [2], that it is in the form of a colloidal solution of TiO_2 in H_2SO_4, and still others [3], that it is in the form of soluble dimers and short-chain linear polymers $[TiO(OH)_2]_2 \cdot 4H_2O$ or $[TiO(OH)_2]_2 \cdot nTiO_2 \cdot (4+2n)\ H_2O$. The latter form at room temperature during the rapid aging (30-60 min) of freshly prepared $Ti(SO_4)_2$ solutions. The rapid aging of the molecularly disperse hydrogel of TiO_2 is also illustrated by the decrease in the dialysis rate of $Ti(SO_4)_2$ solutions and by the considerable decrease in the H_2TiO_3 precipitate volume we observed during the first hour after precipitation and the insignificant subsequent aging in the next two hours. Thus, up to now no complete picture has existed on the state of titanium in different sulfuric acid solutions. However, Kasimov gives interesting data [4] on the composition of the final product from the hydrolysis of $Ti(SO_4)_2$ or the action of alkali on it. According to this author, at 25° the final product from the hydrolysis of $Ti(SO_4)_2$ or the action of alkali on it is not a precipitate with the composition $Ti(OH)_4$ or H_4TiO_4, but two forms of the metaacid (H_2TiO_3): the α form is the freshly precipitated substance that is readily soluble in dilute acids and the β form is the aged substance that is insoluble in acids and retains its composition when heated. Hydrolysis of $Ti(SO_4)_2$ at 60 to 100°, however, gives the acid-insoluble dititanic acid ($H_2Ti_2O_5$).

It seems to us that the chemistry of the system we investigated by the method of solubility and measurement of the apparent precipitate volume is as follows. If one considers that $Ti(SO_4)_2$ is already completely hydrolyzed when it dissolves [2] and that TiO_2 is in a colloidal state in a sulfuric acid medium, then the mechanism of

titanium precipitation by alkali is reduced to the neutralization of H_2SO_4 by alkali. Apparently, the coagulation of previously formed colloidal particles of metatitanic acid occurs here. The H_2TiO_3 precipitated in the system occludes H_2SO_4 to give the product $H_2TiO_3 \cdot \chi H_2SO_4$, where $\underline{x}$ increases with an increase in the H_2SO_4 content of the system and decreases, falling to zero, when alkali is added to neutralize the sulfuric acid completely. At the same time, in parallel with the neutralization of H_2SO_4 with alkali and its ready removal from the precipitate (over the range n = 3.2-4.0), there occurs a gradual increase in the precipitate volume. The above is confirmed by the fact that the curves of solubility and precipitate volume at n = 2 (when half of the H_2SO_4 belonging to one $Ti(SO_4)_2$ molecule is neutralized) do not show the formation of a compound with the composition $Ti\,OH)_2SO_4$ or $TiOSO_4$, and the precipitate volume curves also do not show the complete precipitation of titanium from the solution at n = 3.2 (3.3), i.e., before the stoichiometric ratio of n = 4 is reached (at which the precipitate volume reaches a maximum and its composition corresponds to pure H_2TiO_3). From what has been said we may conclude that it is more probable that H_2TiO_3 containing various amounts of coprecipitated H_2SO_4 forms in the system studied rather than basic titanium salts of variable composition, i.e., Kasimov's data are confirmed [4]. Thus, according to the data we obtained, in the case of dilute solutions the mechanism of precipitation consists of three stages.

1. When n = 0.0−3.2 (3.3) (when all the titanium is in the precipitate). The sulfuric acid coprecipitates with H_2TiO_3 as an insoluble precipitate with the composition $H_2TiO_3 \cdot \sim 0.15\ (0.25)\ H_2SO_4$

$$Ti(SO_4)_2 + 3H_2O \xrightarrow{Na_2SO_4} H_2TiO_3 \cdot 0{,}15H_2SO_4 + 1{,}85H_2SO_4$$

$$Ti(SO_4)_2 + 3{,}2NaOH \longrightarrow H\,TiO_3 \cdot 0{,}15H_2SO_4 + 1{,}6Na_2SO_4 + 0{,}25H_2SO_4 + 0{,}2H_2O.$$

Thus, normal titanium sulfate $Ti(SO_4)_2$ is hydrolyzed in the absence of excess free H_2SO_4 to give a metatitanic acid precipitate containing coprecipitated H_2SO_4 and H_2SO_4 in solution and, in the presence of the latter, it is precipitated completely at n = 3.2 (3.3).

2. n = 3.3 (3.4)−4.0. The reaction occurs in the solid phase with a gradual decrease to zero of the H_2SO_4 in the precipitate as it is neutralized with NaOH.

$$H_2TiO_3 \cdot 0{,}15H_2SO_4 + 0{,}3NaOH \longrightarrow H_2TiO_3 + 0{,}15Na_2SO_4 + 0{,}3H_2O.$$

3. n = 4-5. NaOH coprecipitates with H_2TiO_3 (we must take into account the fact that H_2TiO_3 is a weak acid and after 24 hr of aging it changes into an insoluble form)

$$Ti(SO_4)_2 + 5NaOH \longrightarrow H_2TiO_3 \cdot x NaOH + (1 - x)\,NaOH + 2Na_2SO_4 + H_2O,$$

where $\underline{x}$ varies from 0.00 to 0.46.

It is noteworthy from the practical point of view that neutralization of dilute sulfuric acid solutions of titanium with sodium hydroxide gave Na_2SO_4 which did not coprecipitate or give chemical compounds with the precipitates $H_2TiO_3 \cdot \chi H_2SO_4$ and $H_2TiO_3 \cdot \chi NaOH$, or with pure H_2TiO_3. As in normal titanium sulfate the ratio $2SO_4^{2-} : Ti^{4+} = 4.01$, a considerable part of the titanium in the supernatant solution should be in the form of normal sulfate when this ratio is increased ($n \geq 1$; $H_2SO_4 = 0.0155$ mole/liter and $n \geq 2.3$; $H_2SO_4 = 0.0259$ mole/liter), while titanyl sulfate should predominate when this ratio is decreased ($n < 1$; $H_2SO_4 = 0.0155$ mole/liter and $n < 2.3$; $H_2SO_4 = 0.0259$ mole/liter). The system $Ti(SO_4)_2 - H_2SO_4 - NaOH - H_2O$ was investigated with one starting $Ti(SO_4)_2$ concentration, but with different sulfuric acid concentrations. An increase in the H_2SO_4 concentration of the starting solution resulted in an increase in its content in the precipitate and an increase in $\underline{n}$ at which complete titanium precipitation began i.e., corresponded to an increase in the pH of the start of $H_2TiO_3 \cdot \chi H_2SO_4$ precipitation. The literature data [5] show that titanium precipitated in the form of insoluble hydrolysis products from sulfuric acid solutions of varying concentrations at pH 1.5, 2.0, and 3.0, i.e., at an acidity of 0.0316, 0.0100, and 0.0010 N. Our data show that at n = 3.2 the hydrogen ion concentration at which complete precipitation of titanium as $H_2TiO_3 \cdot 0.15\ H_2SO_4$ started was $6.4 \cdot 10^{-3}$ g-ion/liter, or pH 2.2, while at n = 3.3 complete precipitation of titanium in the form of $H_2TiO_3 \cdot 0.25\ H_2SO_4$ began at pH 2.6. Thus, the literature data are confirmed by our data. The pH at which complete precipitation of $H_2TiO_3 \cdot \chi H_2SO_4$ and H_2TiO_3, as of all the precipitates, started depends on the starting titanium concentration of the solution and the

presence of other salts. An increase in the H_2SO_4 concentration or Na_2SO_4 content of the system studied raised somewhat the pH value at which $H_2TiO_3 \cdot \chi H_2SO_4$ is precipitated. We may conclude from this that an increase in the amount of sulfates in the solution hinders the hydrolysis of $Ti(SO_4)_2$ according to the Law of Mass Action. A decrease in the titanium in a system of constant acidity (sulfate content) apparently also results in a similar increase in the pH of $H_2TiO_3 \cdot \chi H_2SO_4$ precipitation.

The given data indicate that in the capacity for the whole of the cation to precipitate before the stoichiometrically required amount of alkali has been added, titanium is similar to aluminum [6], gallium [7], zinc [8, 9], cadmium [9, 10] thorium [11], neodymium [12], divalent nickel [13], beryllium [14], indium [15], divalent copper and mercury [9], and zirconium [16] and that this phenomenon should be accepted as a general rule for all metals (in analogous systems) forming difficultly soluble bases or acids. Exceptions to this are systems with silver salts and zinc nitrate. Titanium, however, differs from the elements listed above in the fact that through hydrolysis its hydroxide starts to precipitate even before addition of alkali and a much smaller amount of the latter is required for complete precipitation than in the case of other tetravalent elements.

We can also assume that on the basis of work by Tananaev, et al., mentioned above the pH at which metals start to precipitate from their salts under the action of alkali, with the exception of zinc nitrate [9] and silver salts [17], corresponds to their basic salts and not to the hydroxides of these metals. Therefore, the solubility products of hydroxides calculated from the pH of the start of precipitation of pure metal hydroxides, as was done, for example, by Korenman for rare metals and by other authors, are incorrect. As our work showed, what has been stated above may be extended to slightly soluble acids (H_2TiO_3 and probably H_2SiO_3, H_2SnO_3, etc.), the pH of the start of precipitation of which refers not to their pure, but contaminated forms (with substances present in solution; sulfuric acid or NaOH for H_2TiO_3, for example). It is evident that the calculation of solubility product should refer to separately taken pure precipitates without other substances contaminating the precipitates present in solution. As regards the procedure of measuring the apparent precipitate volume proposed by Tananaev, it is less satisfactory in comparison with the one we proposed as manual mixing of the system is necessary and also because the attainment of the equilibrium state in a number of cases requires more prolonged mixing of the system (cf. in Fig. 3 the difference between the precipitate volume curves obtained by our method and by Tananaev's method). Our use of one vessel for work by the two investigation methods, in addition to the attainment of equilibrium in the system, also accelerated the work. The kinetics of precipitation can also be studied by our procedure as well as by Tananaev's. It seems to us that our proposed variant is more efficient because the one vessel serves two purposes and in addition the results obtained are more reliable in cases when the equilibrium in the system is established more or less slowly as occurred in the system we investigated.

SUMMARY

1. It is proposed that chemical systems are investigated by the methods of solubility and apparent precipitate volume simultaneously with the use of the same vessel, which accelerates the work.

2. In the system $Ti(SO_4)_2-H_2SO_4-NaOH-H_2O$ in dilute solutions, the formation of a precipitate as the alkali is increased consists of three stages: 1) coprecipitation of H_2SO_4 with H_2TiO_3, 2) neutralization of the H_2SO_4 in the precipitate with NaOH solution until free H_2TiO_3 is formed, and 3) coprecipitation of NaOH with H_2TiO_3.

3. In actual fact, the pH of the beginning of precipitation of supposed hydroxides of elements, which is used in chemistry at the present time, corresponds in most cases to the pH of the beginning of precipitation of basic or acidic salts of these elements.

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ADSORPTION OF VAPOR ON ADSORBENTS WITH HETEROGENEOUS SURFACES

COMMUNICATION 1. EXPERIMENTS WITH SILICA GELS WHOSE HYDROXYL GROUPS ARE PARTIALLY REPLACED BY FLUORINE ATOMS

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The thoery of Brunauer, Emmett, and Teller (BET), which was developed for adsorbents with an energetically homogeneous surface, is usually used for determining the specific surfaces of nonporous and porous adsorbents [1]. With a series of simplifying assumptions, this theory leads to the adsorption isotherm equation:

$$a = \frac{a_m ch}{(1-h)[1+(c-1)h]}, \tag{1}$$

where a is the amount of adsorption at the equilibrium relative pressure $h = p/p_s$ and a_m and c are constants. The constant a_m expresses the amount of adsorption for a close-packed monomolecular layer; the constant c is closely connected with the pure heat of adsorption $q - \lambda$ for the first monomolecular layer:

$$c = e^{\frac{q-\lambda}{RT}}. \tag{2}$$

In formula (2), q is the differential heat of adsorption for the first monolayer, which is considered independent of the filling of the surface in connection with the assumption of its energetic homogeneity; λ is the latent heat of condensation of the vapor to liquid in bulk.

The adsorption isotherm equation (1) is readily reduced to the linear form:

$$\frac{h}{a(1-h)} = A + Bh. \tag{3}$$

The parameters of the line A and B, determined by a graphical method, are used to calculate the constants of the adsorption isotherm equation a_m and c:

$$a_m = \frac{1}{A+B}, \tag{4}$$

$$c = \frac{A+B}{A}. \tag{5}$$

The determination of the specific surface of the adsorbent s is based on the assumption that the molecular area in a close packed monolayer, ω, is constant. In this case:

$$s = a_m \omega N, \tag{6}$$

where N is the number of molecules per millimole or micromole of substance, in accordance with the units adopted for expressing the amount of adsorption (mmole/g or μmole/g).

TABLE 1

Basic Data on the Properties of the Silica Gels Obtained

Silica gel	s in m^2/g	r_m in A	v_s in cm^3/g	OH in mE/g	in $\mu E/m^2$
SC	326	65	1,610	2,88	8,83
SF	642	20,5	0,615	4,10	6,38

TABLE 2

OH Group Content of Silica Gel Samples

Silica gel sample	OH in mE/g	Relative OH group content	s in m^2/g with $\omega = 16.2$ A^2	OH in $\mu E/m^2$
SC	0,99	1,00	326	3,03
SC1	0,68	0,69	278	2,44
SC2	0,40	0,40	236	1,69
SF	1,22	1,00	642	1,90
SF1	0,69	0,57	632	1,09
SF2	0,32	0,26	548	0,59

Nitrogen at its boiling point (-195°) is usually used as a standard vapor for measuring adsorption. Nitrogen is a nonpolar substance and reacts to a small extent on the chemical state of the adsorbent surface [2, 3]; its molecules are relatively small in size and even for relatively finely porous adsorbents, practically no increase in the adsorption potentials in the pores is observed [4]. We should also note a number of procedural advantages in measurements of adsorption isotherms of nitrogen vapor. However, in addition to nitrogen, a number of other substances in the vapor state are widely used for determining the specific surfaces of adsorbents in practice; these include the noble gases, carbon dioxide, water, aliphatic and aromatic hydrocarbons, etc.

The main assumption in the Brunauer, Emmett, and Teller theory of polymolecular adsorption, namely, the energetic homogeneity of the adsorbent surface, is hardly ever justified for real adsorbents due to the chemical inhomogeneity of the structure of their surface. With relatively finely porous adsorbents, the energetic inhomogeneity of the surface is increased due to an increase in the adsorption potentials in the fine pores of the adsorbents. As a result, despite the formal applicability of the Brunauer, Emmett, and Teller adsorption isotherm equation and the possibility of calculating the constants a_m from formula (4), the determination of the specific surface of the adsorbents from formula (6) becomes extremely conditional due to the indeterminate value of the molecular area ω in this case.

If the adsorbent is quite coarsely porous or completely nonporous and its surface is chemically homogeneous, though there is a discrete structure only on molecular scales, then with a certain approximation, the main assumption in the Brunauer, Emmett, and Teller theory may be considered physically justified. Typical examples are nonporous preparations of silica or coarsely porous silica gel with maximum hydration of the surface. In this case the surface of the adsorbent actually consists of hydroxyl groups and judging by crystallographic data, each of these corresponds to an area of 13.5-14.5 A [5].

From the theoretical and procedural points of view, it is of fundamental importance to determine directly

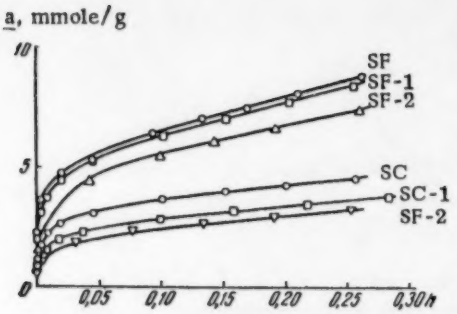

Fig. 1. Isotherms for the adsorption of nitrogen vapor at - 195° by silica gel samples of the SC and SF series.

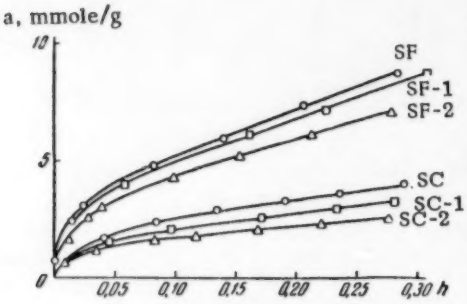

Fig. 2. Isotherms for the adsorption of argon vapor at -195° by silica gel samples of the SC and SF series.

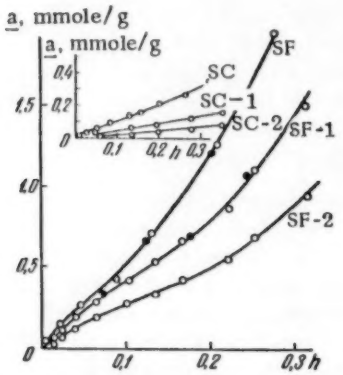

Fig. 3. Isotherms for the adsorption of cyclohexane vapor at 20° on silica gel samples of the SC and SF series.

the molecular areas for close-packed monolayers of adsorbed vapors of various substances on the surface of adsorbents whose chemically homogeneous structure is disrupted by the partial replacement of the true surface radicals by other radicals. This problem may be solved by studying the equilibrium adsorption of various vapors on adsorbents both in the initial state and with chemically modified surfaces.

The most suitable subjects for such an investigation are undoubtedly silica gels, the chemical state of whose surface has been studied quite well [5]. Methods are known for the chemical modification of their surface without an appreciable change in the porous structure [6, 7]. Since the most appreciable change in the adsorption properties of silica gels is produced by replacing the surface hydroxyl groups by fluorine atoms, i.e., by fluorination of silica gels, this method of chemical modification of the surface was adopted in the present investigation.

EXPERIMENTAL

1. Two silica gel samples were used for the experiments: homogeneously coarsely porous (arbitrarily denoted by SC) and homogeneously finely porous (arbitrarily denoted by SF). The starting samples of silica gel were prepared under laboratory conditions by precipitation from sodium silicate solutions with sulfuric acid; their porous structure was controlled by changing the pH of the water used for washing the hydrogel [8]. The SC sample was obtained from a hydrogel washed free from salts with water with pH 8.2, while in the case of sample SF, the pH was 5.5. In addition, the hydrogel of sample SC was subjected to strong dehydration with concentrated sulfuric acid.

Table 1 gives the main data on the properties of the starting silica gels on the basis of isotherms for the low temperature sorption and desorption of nitrogen vapor. In the calculation of the specific surface of the silica gels s, the molecular area for nitrogen was taken as $\omega = 16.2\ A^2$. A correction for the thickness of the adsorption layers was introduced into the calculation of the effective radii r_m for the maxima of the pore volume distribution curves. The limiting sorption volumes are denoted by v_s. The content of hydroxyl groups in the silica gels was determined by a thermal method.

Silica gel samples with various degrees of replacement of the hydroxyl groups by fluorine atoms were obtained by treating the starting silica gels SC and SF with solutions of hydrogen fluoride in absolute ethanol. The hydrogen fluoride concentrations were varied from 2 to 5 vol. %. A portion of silica gel was covered with a solution of hydrogen fluoride in ethanol and kept in it for an hour at room temperature with periodic stirring. The silica gel was separated from the solution and dried on a water bath until the evolution of hydrogen fluoride ceased. The samples were finally dried at 170° in a drying cupboard. In this way two samples each with chemically modified surfaces were obtained from the starting silica gels SC and SF.

2. To determine the amount of hydroxyl groups in the silica gels chosen for investigation, we used Berger's method [9], which was applied to silica gels in [10]. This method consists of converting the acid hydroxyl groups of silica gel to methoxyl groups and then determining them by the Zeisel method [11, 12]. The methylation

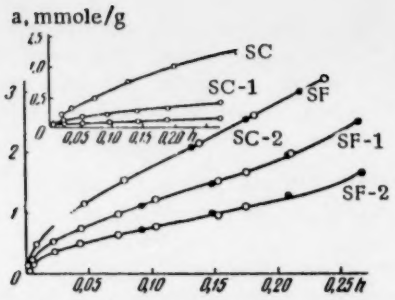

Fig. 4. Isotherms for the adsorption of benzene vapor at 20° by silica gel samples of the SC and SF series.

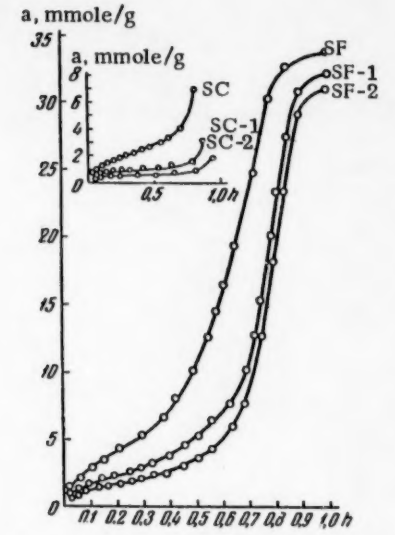

Fig. 5. Isotherms for the adsorption of water vapor at 20° by silica gel samples of the SC and SF series.

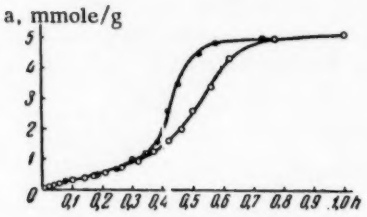

Fig. 6. Isotherm of the sorption and desorption of cyclohexane vapor at 20° on SF2 silica gel.

was carried out with an ether solution of diazomethane, obtained from nitrosomethylurea. The solution was replaced by a fresh one every 4 hr. The reaction was considered complete when gas bubbles were no longer evolved when the solution was added and the yellow color of diazomethane did not disappear overnight. The methylated silica gel sample was separated from the solution, washed several times with absolute ether, and dried in a vacuum drying cupboard at 110°. The analysis results are given in Table 2. In the calculation of the OH group content per unit surface of the adsorbents, we used the specific surfaces determined from the low-temperature adsorption of nitrogen.

In Table 2 the silica gel samples of each series are arranged in the order of decreasing hydroxyl group content. A comparison of the data in Tables 1 and 2 on the OH group content of the starting silica gels shows that the methoxylation method made it possible to determine only 34-30% of the hydroxyl groups. Qualitatively analogous results were obtained in other investigations [6, 10]. Thus, from the results of the analyses it is only possible to estimate the relative content of hydroxyl groups in the silica gel samples obtained.

3. As the substances for adsorption we chose nitrogen, argon, cyclohexane, benzene, and water of a high degree of purity. Sorption balances [13] were used for measuring the adsorption isotherms for nitrogen and argon vapor at -195°; the sorption isotherms for cyclohexane, benzene, and water vapor at 20° were determined analogously, but on another apparatus. The adsorbents were first evacuated at 150°.

Nitrogen and argon are examples of nonpolar substances; their molecules are relatively small in size. The adsorption of vapor of these substances is the result of the appearance of only disperison forces and for silica gel samples of the SC and SF series there was practically no increase in the adsorption potentials in the pores of the adsorbents [4]. Cyclohexane is also a nonpolar substance; its molecules are larger and have a more complex space configuration. One would expect an increase in the adsorption potentials of cyclohexane in the pores of silica gels of the SF series [14]. The adsorption of benzene vapor is determined not only by dispersion forces but also by an interaction of a donor–acceptor nature of benzene molecules with OH groups of the silica gel surface [15]. The adsorption potentials caused by the dispersion components of the adsorption forces will increase in the pores of silica gels of the SF series [16, 14]. Finally, for water the adsorption is mainly the result of the appearance of hydrogen bonds between the water molecules and the hydroxyl groups of the silica gel surface. In this case the adsorption forces are chemical in nature and the effect of an increase in the adsorption potentials in the silica gel pores is practically absent. Thus, the substances chosen for investigation make it possible in principle to determine the characteristics of the chemical state of the surface of the silica gel samples obtained.

4. Figures 1-5 show graphically the adsorption regions of the isotherms for all the vapors studied on the silica gel samples of the SC and SF series. According to Figs. 1 and 2, the adsorption isotherms for nitrogen and argon vapors are convex curves, which are analogous in form in general. In connection with the substantially greater adsorbability of nitrogen vapor, the isotherm curves rise more steeply in the region of low

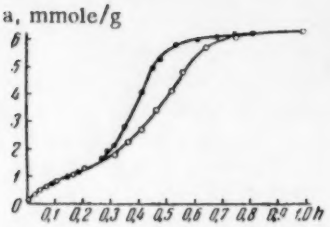

Fig. 7. Isotherm of the sorption and desorption of benzene vapor at 20° on SF2 silica gel.

equilibrium pressures. In accordance with the smaller specific surface of SC silica gels in comparison with SF silica gel, the adsorption isotherms for silica gel samples of the SC series lie considerably lower. The effect of chemical modification of the silica gel surface was not too substantial and was qualitatively analogous for adsorption isotherms of nitrogen and argon.

Cyclohexane vapor was adsorbed relatively little on silica gel samples of the SC series (Fig. 3) and the effect of chemical modification of the silica gel surface was very considerable. The initial sections of the adsorption isotherms were almost linear. The change to the more finely porous silica gel SF was accompanied by a considerable increase in the adsorption of cyclohexane vapor. The initial sections of the adsorption isotherms were slightly convex curves (Fig. 3). The effect of chemical modification of the surface of SF silica gel on the adsorption of cyclohexane vapor was more appreciable than onthe adsorption of nitrogen and argon vapors, but considerably less than in the adsorption of cyclohexane vapor on silica gels of the SC series.

TABLE 3

Limiting Sorption Volumes

Vapor	Silica gels of SC series			Silica gels of SF series		
	sample	a_s in mmole/g	v_s in cc/g	sample	a_s in mmole/g	v_s in cc/g
N_2	SC	46,4	1,61	SF	17,7	0,61
Ar		—	—		21,6	0,61
C_6H_{12}		15,1	1,63		5,60	0,60
C_6H_6		18,5	1,64		6,91	0,61
H_2O		84,5	1,52		33,7	0,62
N_2	SC-1	47,3	1,64	SF-1	17,8	0,62
Ar		—	—		21,3	0,60
C_6H_{12}		15,0	1,62		5,47	0,59
C_6H_6		18,5	1,64		6,54	0,58
H_2O		49,9	0,89		32,2	0,58
N_2	SC-2	46,8	1,62	SF-2	17,0	0,59
Ar		—	—		21,2	0,60
C_6H_{12}		14,8	1,60		5,15	0,56
C_6H_6		17,6	1,57		6,19	0,55
H_2O		29,7	0,53		31,1	0,56

The isotherms for the adsorption of benzene vapor on silica gels of the SC and SF series are represented graphically by convex curves (Fig. 4). We should again note the considerably lower adsorption capacity of silica gel samples of the SC series in comparison with silica gels of the SF series. The adsorption isotherms of SF samples rose steeply in the region of low equilibrium pressures. The effect of chemical modification of the surface was considerable and was greater for silica gels of the SC series.

The isotherms for the adsorption of water vapor on silica gels of the SC and SF series had a characteristic sigmoid form with convex initial sections (Fig. 5). In contrast to previous graphs, Fig. 5 shows sorption isotherms of water vapor for a wider range of equilibrium relative pressures and, in particular, right up to h=1 for the silica gels of the SF series. Chemical modification of the silica gel surface led to a substantial decrease in the amount of adsorption in the initial sections of the isotherms and a displacement of the regions of relative pressures corresponding to the sharp rise of the middle sections of the curves toward higher pressures. Again the effect of modification of the surface appeared to a greater extent with silica gel samples of the SC series.

Thus, replacement of some of the surface hydroxyl groups of silica gels by fluorine atoms leads to a decrease in their adsorption capacity with vapors of all the substances studied. This change in activity is greater with substances for which a substantial part of the adsorption interaction is played by the donor–acceptor component (water and benzene) and is much less with nonpolar substances for which there is only a dispersion

TABLE 4

Specific Surfaces of Adsorption Films for the Beginning of Irreversible Capillary Condensation

Vapor	Silica gels of SC series			Silica gels of SF series		
	sample	h_*	s' in m^2/g	sample	h_*	s' in m^2/g
C_6H_{12}	C	0,68	338	F	0,25	398
	C1	0,68	283	F1	0,25	383
	C2	0,68	283	F2	0,25	357
C_6H_6	SC	0,68	325	F	0,23	369
	SC1	0,68	331	F1	0,23	388
	SC2	0,68	268	F2	0,23	367

TABLE 5

Constants of the BET Equation for the Silica Gels Studied

Vapor	Silica gels of SC series				Silica gels of SF series			
	sample	a_m in mmole/g	c	range of h	sample	a_m in mmole/g	c	range of h
N_2	SC	3,35	119	0,02—0,38	SF	6,58	69,2	0,07—0,40
Ar		3,08	27,0	0,04—0,35		7,24	15,3	0,07—0,42
C_6H_{12}		0,400	2,62	0,05—0,25		0,922	7,75	0,02—0,11
C_6H_6		1,03	11,4	0,04—0,30		2,96	10,2	0,08—0,20
H_2O		1,74	11,3	0,05—0,32		4,47	11,8	0,05—0,35
N_2	SC1	2,86	102	0,02—0,25	SF1	6,49	67,0	0,02—0,35
Ar		2,52	26,4	0,04—0,35		6,78	17,7	0,05—0,32
C_6H_{12}		0,175	2,40	0,10—0,35		0,895	6,69	0,02—0,14
C_6H_6		0,343	13,7	0,06—0,35		1,97	10,7	0,07—0,20
H_2O		0,642	55,8	0,05—0,32		2,34	15,8	0,05—0,33
N_2	SC2	2,42	91,6	0,03—0,34	SF2	5,62	65,8	0,04—0,35
Ar		2,08	26,7	0,05—0,35		5,99	14,5	0,08—0,35
C_6H_{12}		0,083	2,83	0,10—0,35		0,701	4,95	0,04—0,18
C_6H_6		0,134	12,9	0,05—0,30		1,35	9,90	0,05—0,22
H_2O		0,421	39,7	0,05—0,30		1,70	16,8	0,07—0,35

interaction (nitrogen and argon). The behavior of cyclohexane, which reacts sharply on the chemical state of the silica gel surface, is unexpected. In the general case, the described change in the adsorption capacity of silica gel samples when some of their surface hydroxyl groups are replaced by fluorine atoms may be the result of the change in the chemical nature of the surface of the silica gels and in their porous structure. Therefore, for a more unequivocal analysis of the experimental data, it was necessary to assess the possible change in the porous structure as a result of the preparation of the modified silica gel samples.

5. The nature of the change in the porous structure of silica gel samples of each series could be assessed from curves of the distribution of pore volume with respect to size, calculated from the desorption branches of isotherms for capillary condensation of vapor. This method requires very detailed study of the desorption branches of the isotherms and laborious calculations. A simpler and no less strict a method, which was used in [6], is an examination of two quantitative characteristics of the porous structure, namely, the limiting sorption volume and the specific surface of the adsorption film for irreversible capillary condensation. Semiquantitative conclusions may also be drawn by comparing hysteresis loops of the sorption isotherms.

Table 3 gives values of the limiting sorption volumes of various vapors at $\underline{h}=1$ for all the silica gel samples studied; tabular values of the densities of the liquids of the corresponding substances were used for calculating them from the limiting sorption values.

TABLE 6

Experimental Values of Molecular Areas for Close-Packed Monolayers

Adsorbent	ω in A²			
	Ar	C_6H_{12}	C_6H_6	H_2O
SC	17,6	136	52,7	31
SC1	18,4	265	135	72
SC2	18,8	472	292	93
SF	14,7	115	36	24
SF1	15,5	117	53	45
SF2	15,2	130	67	54

The limiting sorption volume for each silica gel sample was practically constant and independent of the nature of the vapor. An exception was found with water vapor and silica gels of the SC series. Treatment of the silica gels for chemical modification of their surface was accompanied by a slight decrease in the limiting sorption volume.

Isotherms of the sorption and desorption of cyclohexane and benzene vapor were used for calculating the specific surfaces of adsorption films for the beginning of capillary condensation of vapor (beginning of hysteresis). As an example, Figs. 6 and 7 show these isotherms for the silica gel SF2. The hysteresis loops for other samples of the SF series were almost the same in form and dimensions. An analogous picture was observed for samples of the SC series. The specific surfaces of the adsorption films s' were calculated by the method in [17]; the results are given in Table 4, where h_0 is used to denote the relative pressures at the points at the beginning of hysteresis.

According to the data in Table 4, the mean values of the specific surfaces of the adsorption films were $s' = 303 \pm 35$ m²/g for SC samples of silica gel and $s' = 377 \pm 20$ m²/g for the SF series. The magnitudes of the deviations were close to 10%.

The specific surface of the adsorption film for samples of coarsely porous silica gels of the SC series was only slightly less than the specific surface of the starting SC silica gel, $s = 326$ m²/g, determined from the low-temperature adsorption of nitrogen vapor. A considerably greater difference was observed for silica gels of the SF series ($s = 642$ m²/g and $s' = 377$ m²/g). According to the idea of the globular structure of silica gels, their skeleton consists of nonporous, spheroidal primary particles and the pores are the spaces between these particles [18]. In the first approximation these spaces may be considered as pores with a spherical form. With a radius of spherical pores of $r = 20.5$ A it is sufficient to have an adsorption film thickness of $l = 4.8$ A for the ratio of $s/s' = 1.70$ to be observed, as was found for the SF silica gels. For benzene, the experimental value $l = 3.0$ A at 20° and $h_0 = 0.25$. If it is assumed that $r = 65$ A and $s/s' = 1.07$ (SC silica gels), then the calculated value $l = 2.5$ A. On the whole, the specific surfaces of the adsorption films found agree with the specific surfaces of the silica gel skeletons.

Thus, treatment of the silica gel samples for chemical modification of their surface did not lead to any essential change in their porous structure in comparison with the starting samples. Therefore, the observed differences in the adsorption properties were mainly caused by the change in the chemical nature of the silica gel surface.

6. The adsorption isotherms of the vapors studied corresponded quite well to equation (1) of the Brunauer, Emmett, and Teller theory. This made it possible to calculate the equation constants a_m and c for all the vapor–adsorbent systems studied. Table 5 gives the values of the constants and the relative pressure ranges over which equation (1) describes the experimental data.

Over the given ranges of applicability of the equation, the amounts of adsorption of vapor calculated by equation (1) by means of the constant a_m and c from Table 5 did not show a deviation from the experimental values of more than 5%. The greatest deviations, which reached 10%, were observed for individual points of the isotherm for the system C_6H_{12}–SC1. For all vapors with the exception of cyclohexane, the equilibrium relative pressures h_m

$$h_m = \frac{\sqrt{c} - 1}{c - 1} \qquad (7)$$

corresponding to the adsorption values according to equation (1), lie within the limits of applicability of the equation given in Table 5. In the case of cyclohexane, the values of h_m lie beyond these limits in regions of higher relative pressures.

The nature of the change in the constants a_m as a result of chemical modification of the silica gel surface

is in general qualitative agreement with the change in adsorbability of the vapors described above. These changes are relatively less marked for nitrogen and argon vapors and more appreciable for the other vapors studied. The changes in the constants c are less regular both as a result of replacement of the surface hydroxyl groups of silica gels by fluorine atoms and with a change from coarsely porous samples of silica gels to more finely porous samples.

DISCUSSION OF EXPERIMENTAL RESULTS

The experimental data presented show that in general the observed change in the adsorption properties of silica gels after chemical modification of their surface is the result of the change in the chemical nature of the surface. In addition to this, we cannot ignore the slight tendency for a decrease in the limiting sorption volumes (Table 3) and specific surfaces of the adsorption films (Table 4) with a change from the starting samples of SC and SF silica gels to samples SC2 and SF2 with the greatest degrees of replacement of OH groups by fluorine atoms, which indicates an appreciable change in the porous structure of the samples. According to the data in Table 4, the maximum deviations in the specific surfaces of the adsorption films for silica gel samples did not exceed 16-17% for the SC series and 6-10% for the SF series. These ranges apparently also cover the probable changes in the specific surfaces of the samples due to treatment of the silica gels for chemical modification of their surface.

For nitrogen and argon vapors, which react least to the change in the chemical state of the silica gel surface, the change from sample SC to SC2 led to a change in the values of a_m by 28-32% and the analogous changes in a_m with a change from sample SF to SF2 were 15-17%. Thus, these changes are beyond the possible limits of the change in the true specific surfaces of the samples, without mentioning the more considerable changes for other vapors. Therefore, they may be correlated with the change in the chemical nature of the silica gel surface

Partial replacement of the surface hydroxyl groups of silica gels by fluroine atoms led to the formation of adsorbents whose surface was heterogeneous in the chemical sense. This heterogeneity should be reflected by the values of the molecular areas for close-packed monolayers. In our experiments we measured the adsorption isotherms for various vapors and, in particular, for nitrogen, which is a standard substance for determining the specific surfaces of adsorbents. Therefore, it is advantageous to determine directly the molecular areas for various vapors and to correlate them with the change in the chemical nature of the surface of the adsorbents.

If a_m is the constant of equation (1) for the vapor examined, a_m^0 is that for nitrogen, then from the fact that the specific surface of each adsorbent sample is constant we obtained from formula (6) an expression for the molecular area of the vapor in a close-packed monolayer ω, assuming that for nitrogen $\omega^0 = 16.2$ A^2:

$$\omega = 16{,}2\frac{a_m^0}{a_m}\text{A}^2. \qquad (8)$$

Table 6 gives the calculated values of the molecular areas for the adsorption of various vapors on the silica gel samples studied. The constants a_m required for the calculations were taken from Table 5.

According to the data in Table 6, the molecular areas of the substances studied are not constant; they increase to a greater or lesser extent as the surface OH groups are replaced by fluorine atoms and decrease with a change from the coarsely porous silica gel samples of the SC series to more finely porous samples of the SF series. The molecular areas change to the smallest extent for argon and, for the samples of each series, they are close to constant; their mean value for silica gel samples of the SC series $\omega = 18.3$ A^2 and for samples of the SF series $\omega = 15.1$ A^2.

Naturally, the assumption that the molecular area of nitrogen $\omega^0 = 16.2$ A^2 is constant is arbitrary. However, if this assumption is made, then the decrease in the molecular area of Ar with a change to the more finely porous silica gel samples of the SF series may be the result of a slight increase in the adsorption potentials of argon in the finest gaps between the touching primary particles of the silica gel skeleton. This would lead to a certain increase in the values of a_m for argon and, according to formula (8), to a corresponding decrease in the molecular area.

The decrease in the number of hydroxyl groups on the silica gel surface as a result of their partial replace-

ment by fluorine atoms, which in this case are incapable of forming bonds of a donor–acceptor nature, apparently leads to the fact that the dimensions of the molecules do not determine the molecular area and the topography of the chemically heterogeneous adsorbent surface itself becomes the determining factor. On the other hand, the fluorine atoms covering part of the adsorbent surface have a lower polarizability than the hydrogen atoms of the hydroxyl groups or of the hydroxyl groups themselves and this affects the dispersion interaction in the same direction. As a result, the molecular areas of benzene and water increase substantially as the surface OH groups are replaced by fluorine atoms. As has already been noted, the behavior of cyclohexane was unexpected. In this case it appears in the high values of the molecular areas and their considerable increase as the surface of the SC silica gel was modified. The nature of the adsorption interaction of cyclohexane molecules with the surface of the adsorbents studied requires additional experimental and theoretical examination.

The adsorption potentials of benzene and cyclohexane are undoubtedly high in the finer pores of the silica gel samples of the SF series due to the dispersion component of the adsorption interaction. In accordance with what has been stated above, this effect appears as an increase in the values of a_m and, according to formula (8), leads to lower values of the molecular areas and possibly to a relatively smaller change in them with an increase in the degree of replacement of the OH groups by fluorine atoms. There is the possibility that to a certain extent the dispersion component of the adsorption interaction plays an analogous role in the case of water molecules.

Actual adsorbents often have a complex chemical composition and their surface is also heterogeneous in the chemical sense. Natural adsorbents provide a clear example. In such cases great care is required in the selection of the vapors for determining the adsorption isotherms to find the specific surfaces of the adsorbents. For adsorbents with a chemically heterogeneous surface, one should exclude substances that are sensitive to the heterogeneous surface, such as benzene and water, for example.

In a subsequent communication of the present series we will return to a more detailed analysis of the reasons for the change in the adsorption capacity of silica gels with chemical modification of the surface.

SUMMARY

1. Replacement of some of the hydroxyl groups on the surface of silica gels by fluorine atoms leads to a fall in the adsorption capacity of the gels for vapors and to a substantial increase in the molecular areas for filled monomolecular layers.

2. In selecting adsorbates for determining the specific surfaces of actual adsorbents, one should exclude substances that are sensitive to the chemical heterogeneity of the surface.

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SORPTION OF SULFATE COMPLEXES OF ZIRCONIUM BY A HIGHLY ALKALINE ANION-EXCHANGE AGENT

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In the presence of sulfate ions, zirconium forms a series of complexes with various compositions, depending on the hydrogen ion concentration. The formation of these compounds may be represented by the general scheme

$$Zr(OH)_n^{+4-n} + mHSO_4^- \rightleftharpoons [Zr(OH)_x(SO_4)_m]^{+4-x-2m} + (n-x)H_2O + (x-n+m)H^+, \quad (1)$$

which shows that the complex examined may have various charges from +2 to -4. The presence of sulfate groups reduces the affinity of zirconium for hydroxyl groups and therefore it may be assumed that with a sufficient concentration of hydrogen ions, there arises the complex with the composition $[Zr(SO_4)_m]^{+4-2m}$. In a study of the extraction of a zirconium complex with thenoyltrifluoroacetone into organic solvents [1] and the sorption of zirconium from a sulfuric acid medium by a highly acid cation-exchange agent [2], it was established that with an acid concentration below 0.5 M, the zirconium in the solution was mainly in the form of a complex with a positive or zero charge and its composition could be represented by the formulas: $(ZrSO_4)^{2+}$, $[Zr(SO_4)_2]$.

With an increase in the concentration of the complex-forming component, the higher members of the series, i.e., compounds with a negative charge, will be more stable and when these compounds come in contact with a highly alkaline ion-exchange resin one can expect the following exchange reactions [2, 3]:

$$m-(2(RNH_4)_2SO_4 + [Zr(SO_4)_m]^{+4-2m} \rightarrow (m-2)SO_4^{2-} + (RNH_4)_{2m-4}Zr(SO_4)_m,$$
$$(2m-4)RNH_4SO_4H + [Zr(SO_4)_m]^{+4-2m} \rightarrow (2m-4)SO_4H^- + (RNH_4)_{2m-4}Zr(SO_4)_m, \quad (2)$$

which may occur, however, with the condition that $m > 2$.

In addition to the sorption scheme presented above, as in the case of uranium [3], in principle there is another possible sorption scheme in which a sulfate group bound by the ion-exchange resin participates in the complex formation:

$$2RNH_4SO_4H + (ZrSO_4)^{2+} \rightarrow (RNH_4)_2Zr(SO_4)_3 + 2H^+,$$
$$RNH_4SO_4H + [Zr(SO_4)_2] \rightarrow RNH_4[Zr(SO_4)_3]^- + H^+, \quad (3)$$

and this may explain the sorption of complexes formed at low sulfuric acid concentrations. Both sorption processes depend on the equilibrium state of complex formation and the corresponding equilibrium constant, while

the complex-formation equilibrium is affected by the equilibrium of the exchange of sulfate ions and complex anions on the ion-exchange agent.

The sorption of zirconium on an anion-exchange agent was investigated through a study of the changes in the equilibrium distribution coefficients K_d, whose values were determined from the relation:

$$K_d = \frac{c_r}{c_v},$$

where c_r is the zirconium concentration in the ion-exchange agent, expressed in grams per 1000 g of dry resin, and c_v is the zirconium concentration in the aqueous phase, expressed in grams per 1000 ml of solution.

EXPERIMENTAL

For the experiments we used the highly alkaline phenol–formaldehyde anion-exchange resin AOL in the sulfate form with a sorption capacity of 3.16 mg-equiv/g and a grain size of 0.5-0.25 mm. The experiments were carried out in columns with a cross-sectional area of 1 cm^2. Resin, which had been convertedinto the sulfate form with 2 N sulfuric acid, was packed into the columns to give beds 25 cm in height.

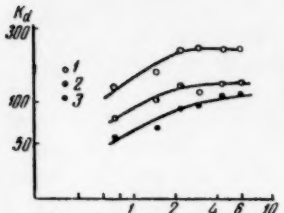

Fig. 1. Relation of K_d to zirconium concentration: 1) 0.75 N sulfuric acid; 2) 1.5 N sulfuric acid; 3) 3 N sulfuric acid.

A standard zirconium solution was prepared in the following way. Zirconium oxide (2.5 g) was converted into the sulfate by fusion with excess potassium bisulfate. The melt was extracted with water and filtered to remove the solid residue. Zirconium hydroxide was precipitated from the heated solution with ammonia. The precipitate was washed until neutral and dissolved in excess hot, dilute sulfuric acid. The solution was diluted to 250 ml. A solution of zirconium in hydrochloric acid was prepared in the same way. The concentration of the standard solutions obtained was checked gravimetrically (by weighing the oxide) and by complexometric titration [4, 5].

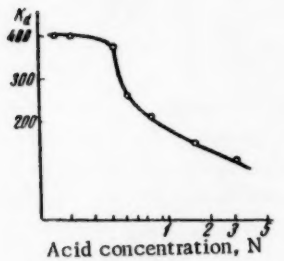

Fig. 2. Relation of K_d to the sulfuric acid concentration.

The distribution coefficients were determined by the usual method from the decrease in the zirconium concentration in the aqueous phase at equilibrium. The change in relation to the initial zirconium concentration and the acid concentration in the solution is shown in Figs. 1 and 2.

To check the hypothesis that the sorption occurs according to scheme 3, we carried out sorption from a hydrochloric acid medium with a resin whose functional groups contained sulfate anion. The results of this experiment did not demonstrate the course of the sorption unequivocally as the sulfuric acid concentration produced by exchange of chloride and sulfate ions between the solution and resin exceeded the initial zirconium concentration in the solution by a factor of 10, even though it was only 10^{-2} M. This experiment confirmed the hypothesis that the upper part of the curve in Fig. 2 was almost parallel to the x axis, i.e., the distribution coefficient depended little on the acid concentration in the solution in this region (Fig. 3). The sharp fall in the distribution coefficient over the range of 0.4-0.7 N acid cannot be explained by the effect of its concentration on the exchange equilibrium, but only by its effect on the composition of the complex in the solution. However, in this region a value of K_d of the order of 10^2 is sufficient for complete sorption of the zirconium with low velocities in the column. If the change in K_d were produced only by the change in concentration of the complex-forming component, i.e., SO_4^{2-} anions, then, if part of these anions are present in the form of a soluble sulfate, a relation similar to that shown in Fig. 2 should be obtained. To check this hypothesis, we investigated the change in the distribution coefficient in 0.5 N sulfuric acid solutions in which the concentration of sulfate anion was increased over the range of 0.1-1.5 N by the addition of sodium sulfate.

The relation obtained, which is illustrated in Fig. 4, shows that sulfates affect the distribution coefficient to a much smaller extent than free sulfuric acid. Therefore, it is most probable that the nature of the curve illustrated in Fig. 2 is affected by the increase in the hydrogen ion concentration.

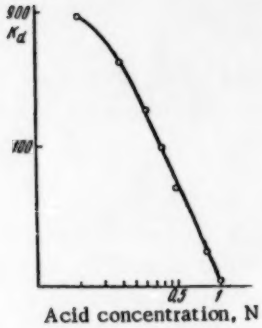

Fig. 3. Relation of K_d to the hydrochloric acid concentration.

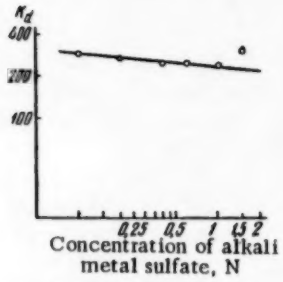

Fig. 4. Relation of K_d to the concentration of alkali metal sulfates.

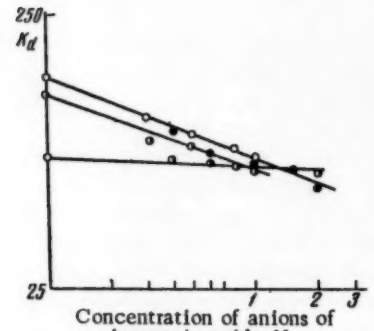

Fig. 5. Relation of K_d to the concentration of anions of inorganic acids: O–0.5N H_2SO_4 + NaCl; ●–0.75N H_2SO_4 + NaCl; ◑–0.5N H_2SO_4 + $NaNO_3$; ◐–0.75N H_2SO_4 + $NaClO_4$.

An investigation was also made of the change in K_d in the presence of anions of other inorganic acids, which were added to the solution as sodium salts. Particular attention was paid to anions of strong acids such as, for example, perchlorate anions, which do not form complexes with zirconium, and also weakly complex-forming anions of chlorides and nitrates. The distribution coefficients were determined by the method described above and the concentration of the foreign anions in the solution varied over the range of 0.05-2 N. The relations obtained show that even at concentration of the order of 10^{-1} N the three anions investigated reduce the value of K_d and their effect increases in the following order: chloride, nitrate, and perchlorate anions. On a logarithmic scale, these relations are linear (Fig. 5).

The changes produced in the presence of chlorides showed that, over definite concentration limits, the value of K_d was independent of the sulfuric acid concentration and only depended on the concentration of the foreign anion. The effect of the anions mentioned above was also investigated under dynamic conditions as a considerable reduction in the value of K_d should be produced by part of the zirconium passing through the column into the eluate. Separate sorption experiments were carried out so that a column of given dimensions retained 46.7 mg of zirconium with a constant flow rate of 1 ml/min from a volume of 50 ml of 0.5 N sulfuric acid, in which the concentration of chlorides and nitrates was varied over the range of 0.2-3 N and of chlorates, over the range of 0.2-2 N. The residual solution was flushed from the resin layer with 20 ml of 0.5 N sulfuric acid and the zirconium in the eluate determined by complexometric titration. The results obtained were used to construct the curves shown in Fig. 6. The change in the experimental conditions had an effect on the form of the lower part of the curves, producing a bend.

Only the upper part of the curves was of important in the determination of the effect of the anions investigated and this showed not only that all three salts caused part of the zirconium to pass through the column, even at a concentration of 0.5 N, but also the increasing effect of the anions investigated in the order given above. It is difficult to explain this satisfactorily. It cannot be assumed that perchlorates form complex compounds as no complex compounds of these salts are known. Complex nitrates and chlorides of zirconium actually exist, but they are much less stable than the corresponding sulfate compounds. The following explanation is more probable: Sorption proceeds according to scheme 3, but as a result of the exchange of ions, the number of sulfate groups in the ion-exchange resin is reduced. This explanation is contradicted by the fact that the equilibrium of such an exchange of ions should be displaced toward the formation of sulfate ions with a ratio of the concentrations of sulfate ions to foreign ions > 1. This hypothesis is supported by the order in which the effect of these anions increases, namely symbatically with an increase in their affinity for ion-exchange resins.

A similar study was made of the effect of organic acids on the sorption of zirconium through the equilibrium distribution coefficients in 0.5 N sulfuric acid containing excess of the organic acid (the acetic acid concentration was varied over the range 0.2-4 M and that of tartaric acid, over the range 0.1-1 M); it was established that acetic acid hardly affects the sorption because there is hardly any dissociation of this acid in a very acid medium. At a high acetic acid concentration there was a very slight increase in the distribution coefficient

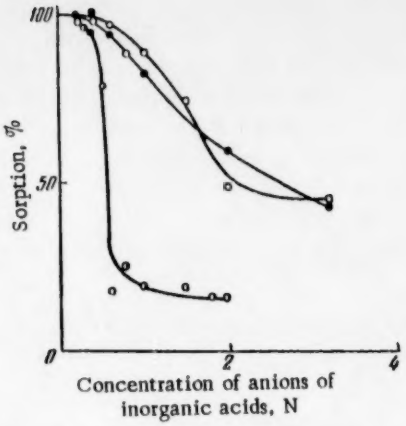

Fig. 6. Effect of anions of inorganic acids on the sorption of zirconium: O—NaCl; ●—$NaNO_3$; ◑—lower curves of $NaClO_4$.

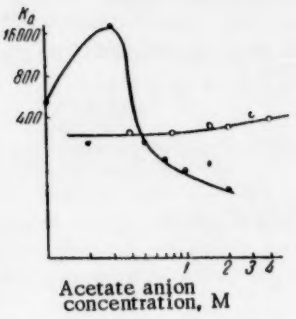

Fig. 7. Relation of K_d to the concentration of acetate anion: O—acetic acid; ● — sodium acetate.

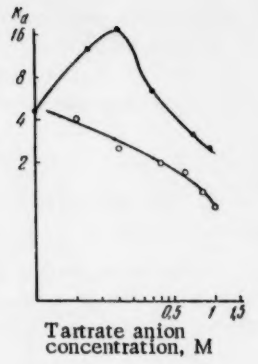

Fig. 8. Relation of K_d to the concentration of tartrate anion: O—tartaric acid; ●—sodium tartrate.

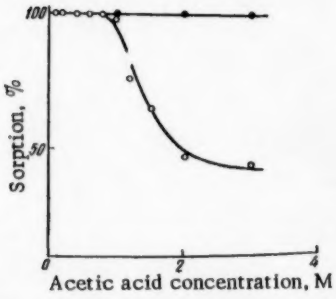

Fig. 9. Effect of an organic acid on zirconium sorption: O—acetic acid; ●—sodium acetate.

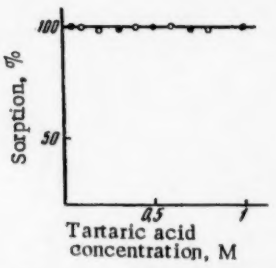

Fig. 10. Effect of an organic acid on zirconium sorption: O—tartaric acid; ●—sodium tartrate.

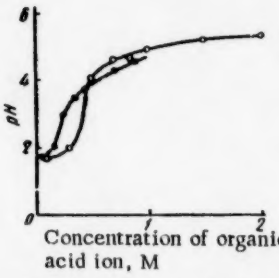

Fig. 11. Change of solution pH with an increase in the concentration of an organic acid ion: O—sodium acetate; ●—sodium tartrate.

(Fig. 7). On the other hand, the presence of tartaric acid increased the distribution coefficient several fold and this was probably produced by sorption of the tartrate complex by the ion-exchange resin (Fig. 8). Experiments with the sorption of 46.7 mg of zirconium on an ion-exchange resin from 50 ml of 0.5 N sulfuric acid containing various amounts of the organic acid (the maximum concentration of acetic acid was 3 M and of tartaric acid, 1 M)demonstrated that in all cases there was quantitative sorption of zirconium (Figs. 9 and 10).

In a study of the effect of alkali salts of organic acids on the sorption of zirconium it was established that alkali salts of organic acids, which are salts of a strong base and a weak acid, affect the sorption mainly by producing an increase in the pH of the solution from which the sorption occurs (Fig. 11). A decrease in the free sulfuric acid concentration in the solution produces an increase in the distribution coefficient up to a definite maximum in accordance with the relation shown in Fig. 2. With a further increase in the organic anion concentration, in both cases there was a fall in the distribution coefficient; over the given concentration range, the acetate anions behaved as a salt of a strong acid and produced a considerable fall in the distribution coefficient (Fig. 7).

Both in the presence of tartaric acid and in the presence of its salt there was sorption of zirconium not as the sulfate complex, but as the tartrate complex; an increase in the tartrate concentration up to 0.2 M also

produced a fall in the distribution coefficient, which occurred as a result of displacement of the tartrate complex by excess tartrate ions (Fig. 8). Over the range of concentrations investigated, which depended on the low solubility of the monosodium tartrate formed, the distribution coefficient reached a value of the order of 10^3, i.e., a higher value than in the sorption of the sulfate complex. Therefore, when a sulfate solution of zirconium containing excess sodium tartrate (over the concentration range 0.1-0.8 M) was passed, it was found that sorption was complete over the concentration range investigated (Fig. 10).

SUMMARY

1. The sorption of zirconium by a highly alkaline anion-exchange agent in a medium of sulfate anions was investigated.

2. It was shown that it is possible to use the sorption of complex compounds of zirconium by an ion-exchange resin for various analytical and preparative purposes in inorganic chemistry. The sorption is extremely selective and the sorbed element may be displaced from the column readily with the normal mineral acids.

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TWO MECHANISMS OF CARBONIZATION IN THE DECOMPOSITION OF BENZENE HOMOLOGS ON SILICA GEL

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At the present time, investigators are becoming increasingly convinced that carbonization under cracking and pyrolysis conditions is polycondensation of starting materials or some of their preliminary conversion products adsorbed on the catalyst [1-8]. Moreover, the opinion that the carbonaceous material formed during the pyrolysis of organic substances is elementary ("pure") carbon, which was introduced by Berthelot [9] and maintained by a number of investigators [10-12], is gradually being replaced by the idea of the carbonaceous material as the product from polycondensation of benzene nuclei or other intermediate compounds [13-20]. In the general case, carbonization is the polycondensation of some starting material and in each actual case there is a specific mechanism, which is determined by the nature of the starting material. This is either dehydrocondensation of benzene [3], butadiene polymerization [2], polycondensation of acetaldehyde [8], or some such process. If there is a change in the starting material for carbonization with a change in the pyrolysis conditions, then there must be a change in the mechanism of this process. One of us observed such a phenomenon previously [3] in the form of two different carbonization mechanisms in the pyrolysis of toluene, o-xylene, and mesitylene, one of which occurred at comparatively low temperatures and the other at high temperatures. Together with this, it was reported that there is only one carbonization mechanism in the pyrolysis of benzene over the same temperature range (500-900°). The present work is a more detailed investigation of this phenomenon on a large number of examples.

EXPERIMENTAL

The experiments were carried out with an automatic flow apparatus for heterogeneous catalytic investigations with an indirect temperature-regulation system [21], which made it easy to select the required temperature and maintain it with an accuracy of ± 0.2° at 800°. The apparatus had a demountable quartz reactor, which made it possible to remove and weight the catalyst and the carbonaceous material formed on it without dismantling the apparatus [3, 22]. The experiments were carried out at 500-900° and atmospheric pressure. The catalyst was 5 ml of KSM grade silica gel, ground to 1-2 mm and purified. A fresh portion of catalyst was used for each experiment. The reacting material (Table 1) was introduced at a rate of 4.78 ml/hr. The duration of each experiment was 2 hr. The apparatus was flushed with nitrogen before and after an experiment. The carbonaceous material was assayed by direct weighing with an accuracy of 0.0001 g and the volatile dehydrocondensation products were determined by analysis of the quantitatively collected catalyzate with an accuracy of 1% of the value determined. In addition, the gaseous products were analyzed on a VTI apparatus and the catalyzates distilled on a fractionating column with an efficiency of 30 theoretical plates. The substances isolated by distillation were identified by the boiling points, refractive indices, and qualitative reactions. The procedure was described in more detail in [3].

TABLE 1

Constants of Starting Hydrocarbons

Starting hydrocarbon	B.p. in °C (p in mm Hg)	d_4^{20}	n_D^{20}
Benzene	79,1 (743)	0,8790	1,5013
Tolune	109,2 (748)	0,8669	1,4965
m-Xylene	135,7—136,2 (749)	0,8649	1,4980
o-Xylene	140,5—141,0 (745)	0,8824	1,5058
p-Xylene	135,5—136,0 (746)	0,8601	1,4964
Ethylbenzene	135,5—136,5 (757)	0,8652	1,4960
Mesitylene	160,5—161,0 (749)	0,8623	1,4996
Cumene	148,7—149,0 (741)	0,8636	1,4918

TABLE 2

Results of Analyses of Catalysis Gases

Starting hydrocarbon	Experiment temperature in °C	Composition of catalysis gases in vol. %		
		hydrogen	unsaturateds	saturateds
Benzene	842	100	0	0
Toluene	636	100	–	–
	690	86	–	14
	786	49	~1	50
m-Xylene	659	100	–	–
	723	95	Traces	5
	787	33	~1	66
o-Xylene	638	100	–	–
	716	92	Traces	8
	784	43	~1	56
p-Xylene	660	~100	Traces	Traces
	722	87	"	13
	789	85	~1	14
Ethylbenzene	639	50	9	41
	717	51	10	40
	845	70	6	24
Mesitylene	842	38	~1	61
Cumene	789	51	8	40

DISCUSSION OF EXPERIMENTAL RESULTS

As Fig. 1 shows, the carbonization rate during the pyrolysis of benzene increased steadily with a rise in temperature, while in the case of toluene, m-xylene, and mesitylene, its increase with a rise in temperature suffered a check in a temperature region which was specific for each of these hydrocarbons and at approximately 7-9% conversion of the starting hydrocarbon to carbonaceous material. The beginning of the check in the increase in carbonization rate for toluene was at 745°, for m-xylene, 695°, and for mesitylene, 660°. If we compare the results of analyses of the catalysis gases (Table 2) and distillation of the catalyzates (Table 3) for experiments at temperatures below and above the "beginning of the check" indicated here, it can be seen that before the beginning of the check in carbonization, methane was practically absent from the catalysis gases and a lower boiling fraction than the original hydrocarbon was practically absent from the catalyzates, while at higher temperatures in the gases there appeared large amounts of methane and in the catalyzates, lower boiling hydrocarbons. The check in the increase in the carbonization rate for benzene homologs was evidently connected with successive demethylation of the hydrocarbons and the formation of lower homologs and finally benzene.

TABLE 3

Results of Distillation of the Catalyzates on a Column

Starting hydrocarbon	Experiment temperature in °C	Composition of catalyzates in weight %				Notes
		benzene fraction	toluene fraction	xylene fraction (ethylbenzene fraction)	residue (dehydrocondensation products)	
Benzene	765	77	0	0	23	
Toluene	688	7	89	0	4	
	785	34	36	0	29	
m-Xylene	650	Traces	7	91	1,6	
	710	3	10	84	4	
	770	9	24	50	17	
o-Xylene	638	1	1	97	1	
	705	1	8	87	4	
	760	10	24	49	18	
p-Xylene	680	1	9	88	2	
	722	4	15	74	7	
	740	12	26	51	12	
Ethylbenzene	639	7	13	79	1	
	717	28	18	25*	30	8% styrene
	743	33	7	18*	35	
Mesitylene	640	Traces	Traces	Traces	1,6	98% mesitylene
	746				17	65% mesitylene
Cumene	640	6	5	14**	15	60% cumene**
	738	28	14	12**	46	2% cumene**

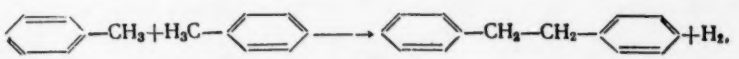
* The ethylbenzene fraction was contaminated with styrene

** The xylene fraction was contaminated with styrene and the cumene fraction with methylstyrene.

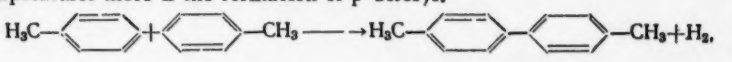
It is also evident that for demethylation to occur it is important that in addition to a definite temperature being reached, there should be a definite degree of conversion of the starting hydrocarbon to carbonaceous material, reaching 7-9% at the "beginning of the check," which is equivalent to the creation of a partial pressure of hydrogen of ~350 mm in the reaction sphere. Consequently, the demethylation observed in the given case is destructive hydrogenation, which occurs due to hydrogen formed during carbonization. Judging by literature data [19, 23-29], destructive hydrogenation of various alkylbenzenes in a mixture with hydrogen proceeds more readily and more extensively the higher the temperature and the hydrogen pressure.

As follows from Fig. 1, with a further increase in temperature above a certain limit, the carbonization rate again began to increase sharply and more or less approached the corresponding values for benzene. If the suppression of carbonization was connected with the demethylation of the starting hydrocarbons, which developed increaseingly with a rise in temperature, then the new activation of carbonization was apparently connected with a change in the mechanism of this process which made possible the dehydrocondensation of benzene formed by demethylation of the starting hydrocarbons, as opposed to their direct dehydrocondensation at lower temperatures.

These conclusions are in agreement with the data of Meyer and Hofmann [30], which showed that in the pyrolysis of toluene at quite low temperatures there is the smooth formation of bibenzyl



and at higher temperatures there is the formation of p-bitolyl.



i.e., at a low temperature the energetic probability of rupture of the $C-H_{aliph}$ bond is higher than that of the $C-H_{arom}$ bond and at high temperature, vice versa.

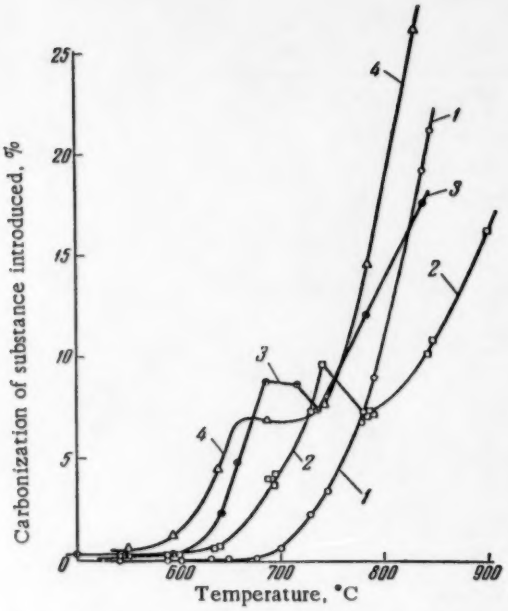


Fig. 1. Temperature dependence of carbonization during the pyrolysis of benzene and alkibenzene on silica gel: 1) benzene; 2) toluene; 3) m-xylene; 4) mesitylene.

In connection with this, the low-temperature carbonization mechanism, which proceeds through direct dehydrocondensation of the starting hydrocarbons, should be represented as successive dehydrocondensations of the starting hydrocarbon with the carbonaceous material through the alkyl substituents, similar to the formation of bibenzyl. The higher energetic probability of such dehydrocondensations in comparison with dehydrocondensations through the benzene nuclei under the conditions of the low-temperature carbonization mechanism of benzene homologs is confirmed by the exceptionally low carbonization rates for benzene itself under these conditions (see Fig. 1).

The high-temperature carbonization mechanism in this case should be represented as successive dehydrocondensations of the starting hydrocarbons or their conversion products with the carbonaceous material through the nucleus, similar to the formation of bitolyl. Such dehydrocondensations become more probable energetically at high temperature as is confirmed by the similarity of the carbonization rates for benzene homologs and benzene itself in the region of the high-temperature mechanism (see Fig. 1). Slight differences in the carbonization rates for benzene and its homologs indicate that the high-temperature mechanism is dehydrocondensation through the nucleus of the starting benzene homologs and their preliminary conversion products, including benzene, and not just dehydrocondensation of benzene obtained by demethylation. In the pyrolysis of benzene itself, the high-temperature carbonization mechanism appears in a pure form and as only dehydrocondensation through the nucleus is possible, there is only the one carbonization mechanism.

The change of the low-temperature to the high-temperature carbonization mechanism is connected with a decrease in the energetic probability of dehydrocondensations between alkyl groups and an increase in the energetic probability of dehydrocondensations between the nuclei of aromatic hydrocarbons, which determine the predominant occurrence of this or that reaction, and is accompanied by the development of hydrogenolysis of the alkyl groups of the starting hydrocarbons.

The existence of two carbonization mechanisms is also confirmed by experiments with o- and p-xylene, ethylbenzene, and cumene. As follows from Fig. 2, a characteristic break in the carbonization curves was observed for all the alkylbenzenes we studied. There are characteristics specific for each hydrocarbon and common characteristics for hydrocarbons of similar structure, which are expressed through the temperature of the beginning of the check in carbonization in different degrees of conversion to carbonaceous material, etc. Thus, xylene isomers hardly differ from each other in these characteristics. For ethylbenzene the temperature of the beginning of the check is the same as for xylenes, but the degree of conversion to carbonaceous material is considerably lower. Cumene shows similar characteristics to mesitylene and cumene and ethylbenzene give practically identical results in the region of the high-temperature mechanism.

The identical temperatures of the beginning of the check in carbonization for the xylenes and ethylbenzene and also for mesitylene and cumene apparently indicate the identical ease of elimination of one methyl group from isomeric substances. In this case the temperature of the carbonization check should be regarded as the temperature limit of the stability of methyl groups of homologs under pyrolysis conditions. One methyl group is removed most readily from mesitylene and cumene (660°), with more difficulty from xylenes and ethylbenzene (695°), and with most difficulty from toluene (745°).

Judging by the composition of the catalysis gases and the catalyzate (see Tables 2 and 3), in the case of ethylbenzene and cumene there is considerable cracking, which is apparently accompanied by the change in

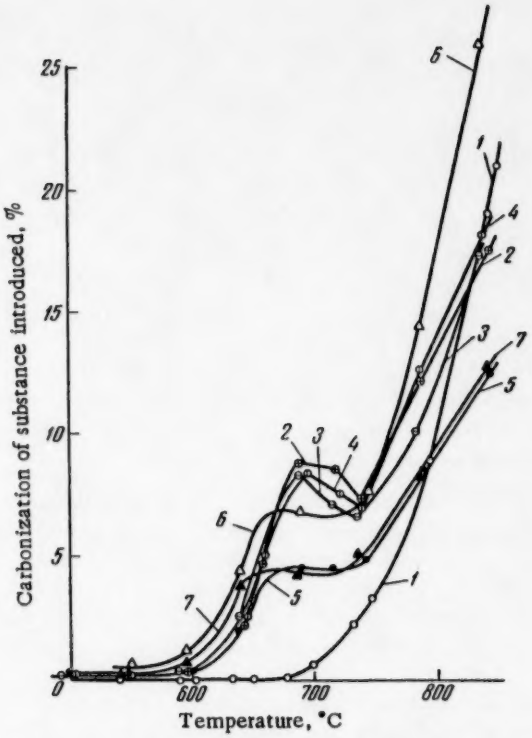


Fig. 2. Temperature dependence of carbonization during the pyrolysis of benzene and alkylbenzenes on silica gel: 1) benzene; 2) m-xylene; 3) o-xylene; 4) p-xylene; 5) ethylbenzene; 6) mesitylene; 7) cumene.

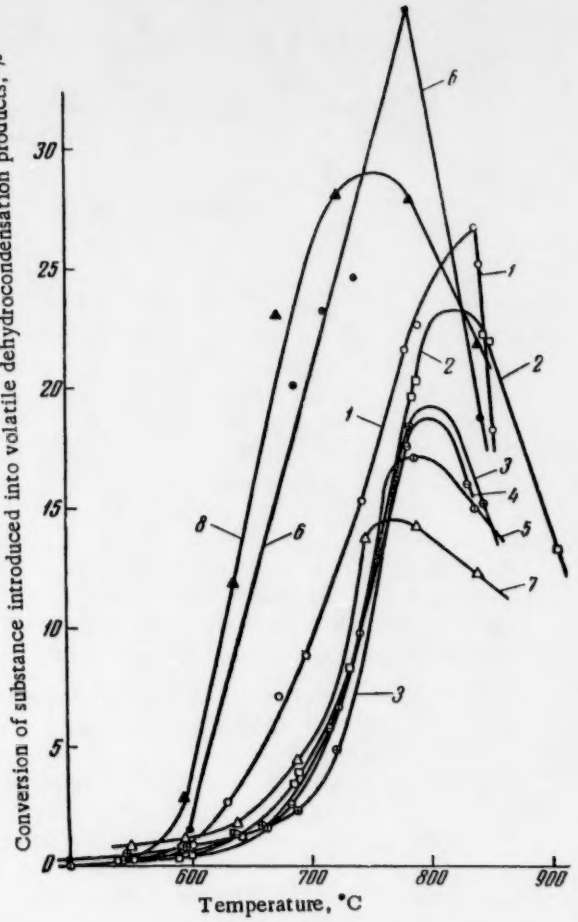


Fig. 3. Temperature dependence of the formation of volatile dehydrocondensation products during the pyrolysis of benzene and alkylbenzenes on silica gel: 1) Benzene; 2) toluene; 3) m-xylene; 4) o-xylene; 5) p-xylene; 6) ethylbenzene; 7) mesitylene; 8) cumene.

the carbonization mechanism and also destructive hydrogenation. Due to the additional role of cracking, the change of the carbonization mechanisms in the case of ethylbenzene and cumene begins at considerably lower degrees of conversion of the starting hydrocarbons to carbonaceous material than in the case of methylbenzenes (see Fig. 2).

The whole of the material examined indicates that carbonization during the pyrolysis of alkylbenzenes and benzene has specific trends for each hydrocarbon. The change in the carbonization mechanism in the case of alkylbenzenes is also caused by the change in the nature of the starting material for carbonization. The presence of one carbonization mechanism in the case of benzene is explained by the retention of the unchanged benzene nucleus and its properties over the whole temperature range studied (500-900°), which is in complete agreement with existing ideas on the special thermal stability of the benzene nucleus [16, 31] and the high strength of the C—C bonds of the nucleus in comparison with C—H bonds [32].

In all the given cases, carbonization is a multistage dehydrocondensation of either the starting hydrocarbons themselves or definite products from their preliminary conversion as only in this case can the specific characteristics of this process reflect the nature of the starting hydrocarbon and its changes, as we have pointed

TABLE 4

Maximum Degrees of Conversion of Benzene and its Homologs to Volatile Dehydrocondensation Products

Starting hydrocarbon	Maximum conversion of hydrocarbon introduced in%	Temperature of maximum in °C
Benzene	27	845
Toluene	24	825
m-Xylene	19	810
o-Xylene	19	810
p-Xylene	17	795
Ethylbenzene	37	790
Mesitylene	14	765
Cumene	29	755

out. Therefore, ideas on carbonization as the decomposition of hydrocarbons to free carbon and hydrogen and also ideas on the formation of carbonaceous material from the simplest free radicals, previously obtained from the decomposing hydrocarbon, must be incorrect. If these ideas were correct we would not observe any specific characteristics in carbonization during the pyrolysis of different hydrocarbons.

In addition to carbonaceous material, the pyrolysis of the hydrocarbons studied yielded volatile dehydrocondensation products, which were carried along with the catalyzate vapor under the experimental conditions and were not incorporated into the "carbonaceous material." According to literature data, the bulk of these products consists of bimolecular dehydrocondensation products (biphenyl, bibenzyl, bitolyl, bixylyl, bimesityl, etc, corresponding to the starting compounds benzene, toluene, xylene, mesitylene, etc.); in addition there were small amounts of products from dehydrocondensation of three, four, and more starting hydrocarbon molecules and some other products [3, 30, 33-37]. Despite the evident genetic connection of these products with the carbonaceous material obtained, according to our ideas, as a result of dehydrocondensation of the same starting materials, the change in the carbonization mechanism was not reflected in the rates of formation of these products (Fig. 3), i.e., the formation of volatile dehydrocondensation products and carbonization proceed independently. The volatile dehydrocondensation products apparently do not play an essential role as starting material for carbonization, i.e., polycondensation occurs mainly at the expense of the starting materials or some of the simpler products of their preliminary conversion.

The rate of formation of volatile condensation products shows quite definite regularities in connection with the structure of the starting hydrocarbons. Attention is attracted by the fact that the rates of formation of volatile products from methylbenzenes are lower than from benzene (see Fig. 3), while one would expect the reverse, considering that the energetic probability of the formation of radicals of benzene and its analogs from methylbenzenes is considerably higher than for the formation of a phenyl radical from benzene [38]. Thus, this fact is not explained by the radical scheme of Rice with the assumption that aromatic radicals are first formed. Free aromatic radicals apparently do not play an appreciable role in the dehydrocondensation reactions and the observed effect may be explained by the fact that, despite the higher energetic probability of bimolecular dehydrocondensation through alkyl groups rather than through the benzene nuclei, this process proceeds at a lower rate due to the low probability of the correct disposition of the reacting molecules. In the case of benzene the lower energetic probability of condensation of the nuclei is compensated by the higher probability of the correct disposition of the molecules. At higher temperatures, bimolecular dehydrocondensation through the nucleus becomes the more favored energetically. This explanation is in complete agreement with the regular fall in the maximum yields of volatile dehydrocondensation products in the series: benzene, toluene, m-, o-, and p-xylenes, mesitylene (see Fig. 3 and Table 4). The sharp fall in the rate of formation of volatile condensation products from ethylbenzene and cumene in comparison with benzene (see Fig. 3) likewise does not support a radical scheme for the reaction as the increase in the rate of formation of condensation products here is quite regularly connected with the possibility of polymerization of the styrene and methylstyrene formed during pyrolysis (see note to Table 3).

SUMMARY

1. There are two carbonization mechanisms in the pyrolysis of alkylbenzenes on silica gel: a low-temperatemperature one (up to 600-745°) and a high-temperature one (at temperatures above 740-785°), which have their own specific characteristics for each hydrocarbon.

2. In the pyrolysis of benzene, carbonization proceeds by only a high-temperature mechanism over the temperature range of 500-900°.

3. In all the cases studied, carbonization is polycondensation (multistage dehydrocondensation) of the starting hydrocarbons and some of their preliminary conversion products. In the low-temperature mechanism, there is dehydrocondensation of the starting alkylbenzenes with the carbonaceous material, predominantly through the alkyl groups; in the high-temperature mechanism, the dehydrocondensation of the starting hydrocarbons and their preliminary dealkylation products proceeds predominantly through the benzene nuclei.

4. The preliminary formation of free aromatic radicals does not play an essential role in the dehydrocondensations.

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REACTIONS OF CYCLOHEXANOL IN CONTACT WITH ACTIVATED CHARCOAL*

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The methods of the multiplet theory make it possible to calculate the sequence of reactions of organic molecules in the presence of a catalyst [2, 3], the energies of the bonds of which with the reagent molecules are known. One such catalyst is activated charcoal, whose adsorption and catalytic properties were studied in the classical investigations of Zelinskii and his co-workers.

There are a large number of papers and patents on the quite universal catalytic properties of carbon (see [4, 5]) and, in particular, its capacity to catalyze dehydrogenation [6-11] and dehydration [8, 12, 13] and to induce irreversible catalysis [1]. The addition of hydrogen to a double bond does not occur up to 500° in the presence of pure charcoal at normal pressure [1].

It should be noted that there are not just carbon atoms on the surface of any pure charcoal. Even at the end of the last century it was reported that oxygen is bound by the surface of charcoal [14]. This phenomenon was later studied in detail by Shilov (see review [15]), Dubinin [16], Frumkin [17, 18] et al., and also by many other investigators [19-23]. The chemisorption of oxygen by charcoal, which, according to Shilov, leads to the formation of surface oxides of an acid or alkaline character, or, according to Frumkin, the formation of a gas electrode, proceeds readily and rapidly, beginning at low temperatures. The preparation of a charcoal surface completely free from oxygen is extremely difficult. The prolonged investigations of Dubinin's school and calculations [16] showed, nonetheless, that in charcoals activated at high temperature the surface oxides constitute approximately 2% of the total surface and this apparently should have no appreciable effect on its catalytic properties in reactions in which all the components are in the vapor phase.

When cyclohexanol is passed in a pure form or together with excess N_2 or H_2, one may visualize quite a large number of reactions in which the starting material is not only cyclohexanol itself, but also its primary conversion products (Table 1).

Most of the reactions listed in Table 1 proceed on two active centers (on a doublet) and only some of them require the presence of either a sextet or two appropriately disposed doublets or triplets. As is known, dehydrogenation on a sextet, as it occurs on Pt, Pd, Ni (atomic radius $r_a = 1.38-1.24$ A), and some other metals, should not occur on charcoal for geometric reasons [24]. However, it is possible to imagine such symmetrical disposition of six-membered rings on a charcoal surface ($r_a = 0.71$ A) when there is present the configuration of active centers (which we assume to be carbon atoms denoted by heavy spots in Fig. 1, that is drawn to scale) necessary to imitate the reaction on a sextet or two triplets.

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*The present investigation, which was carried out under the direction of A.A. Balandin, was begun in 1940 by E.L. Broude and continued by G.I. Levi; the part of the results which was obtained together with N.D. Zelinskii was published in a separate communication [1].

**E.L. Broude was a talented young chemist, trained at Moscow State University, who was killed at the front during the Second World War.

TABLE 1

Sequence of Conversions of Cyclohexanol

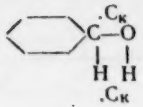
No.	Reaction	Energy barrier, E*, in kcal calculated according to [2]
1	Dehydrogenation of cyclohexanol to cyclohexanone	139.3
2	Dehydration of cyclohexanol to cyclohexene	146.6
3	Irreversible catalysis of cyclohexene on two triplets (calculated for one cyclohexene molecule allowing for the bond strain produced)	≥153.7; < 165.7
4	Dismutation of cyclohexanone by the same mechanism (calculated for one molecule in the enol form)	≥ 153.7; < 165.7
5	Reduction of cyclohexanol with hydrogen to cyclohexane	156.3
6	Codehydration of two cyclohexanol molecules to the ether	156.5
7	Reduction of phenol to benzene with hydrogen	159.3
8	Hydrogenolysis of a C—C bond of the cyclohexane ring	165.7
9	Hydrogenation of cyclohexene to cyclohexane	165.7
	The same allowing for conjugation arising with the "double" bonds of graphite	up to 203.0
10	Dehydrogenation of the cyclohexane ring by the edge mechanism (elimination of the first two hydrogen atoms)	166.5
11	Codehydration of two phenol molecules to the ether	168.6
12	Codehydrogenation of two benzene molecules to biphenyl	171.7
13	Codehydrogenation of two cyclohexane molecules (or cyclohexane and benzene molecules)	176.2
14	Formation of $C_6H_5 \cdot C_6H_5$, $C_6H_{11} \cdot C_6H_{11}$, $C_6H_5 \cdot C_6H_{11}$, through the elimination of H_2O_2 or the formation of hydroperoxides	216—221
15	Hydrogenation of the benzene ring by a doublet or sextet mechanism	> 223
16	Dehydrogenation of the cyclohexane ring bya sextet mechanism, allowing for bond strain produced	≥486
	The same, but without allowing for strain	> 540

In this case we have all the data necessary to calculate the sequence of all the possible reactions from the heights of the energy barriers E* of the desorption stages, which, in accordance with calculation, are considered as limiting the rates. The results of the calculations based on the mean bond energies [25, 26] are also given in Table 1. The degree of double bonding in the graphite was not considered in the calculations (with the exception of reaction 9*).

* Allowing for the degree of double bonding on graphite would lead to a slight increase in the absolute value of E*, especially in the case of reactions 7, 11, 12, 14, and 15.

We take this opportunity to note that the calculation of the sequence of reactions from the height of the energy barrier was proposed by one of us for mono- and quasimonomolecular reactions. In principle, it is also applicable to bimolecular reactions. However, one should remember that, for bimolecular reactions, the result obtained is of a much more approximate nature as it does not reflect additional difficulties (kinetic, steric, and adsorption) connected with a bimolecular mechanism. It is possible that this explains at least partially the high calculated values of E*.

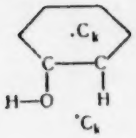
Dehydrogenation of cyclohexanol



$$E^{\circ} = +Q_{C_{\Delta}-O} + Q_{H-H} - Q_{C_{\Delta}-C_{K}} - Q_{O_{\Delta}-C_{K}} - 2Q_{H-C_{K}} =$$

$$= 104{,}7 + 104{,}18 - 73{,}8 - 76{,}9 - 2 \cdot 98{,}75 \approx -139{,}3 \text{ kcal.}$$

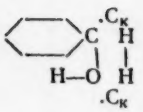
Dehydration of cyclohexanol



$$E^{\circ} = +Q_{H-O} + Q_{C_{\Delta}-C_{\Delta}} - Q_{O-C_{K}} - Q_{H-C_{K}} - 2Q_{C_{\Delta}-C_{K}} =$$

$$= 110{,}8 + 74{,}45 - 85{,}5 - 98{,}75 - 2 \cdot 73{,}8 \approx -146{,}6 \text{ kcal.}$$

Reduction of cyclohexanol with hydrogen



$$E^{\circ} = +Q_{H-O} + Q_{C-H} - Q_{O-C_{K}} - 2Q_{H-C_{K}} - Q_{C-C_{K}} =$$

$$= 110{,}8 + 98{,}75 - 85{,}5 - 2 \cdot 98{,}75 - 82{,}87 \approx -156{,}3 \text{ kcal,}$$

where Q is the mean bond energy, K is the catalyst, and Δ indicates the formation of a three-membered ring.

In the case of reactions 1, 2, and 10 it is necessary to assume that in the adsorption of two bound carbon atoms (or C−O atoms) of a molecule, a three-membered ring is formed at a carbon atom of the catalyst and this unavoidably produces considerable bond strain (see discussion of results). In all these cases, the bond energies of C−C in cyclopropane or C−O in ethylene oxide [26] were used in the calculation. Bond strain also arises in reactions 3, 4, and 16, but its effect on the bond energy can be estimated only very approximately, as is indicated in Table 1.

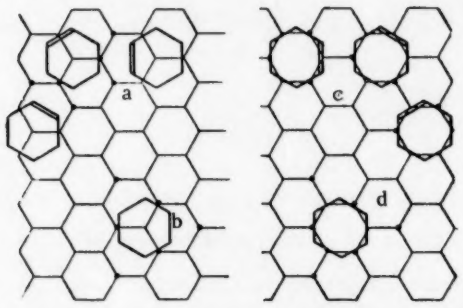


Fig. 1. Schemes for irreversible catalysis of cyclohexene and dismutation of the enol form of cyclohexanone (a), and also the dehydrogenation of cyclohexane (b) on a charcoal surface; c and d are the second possible variants of these schemes, respectively.

As regards the dismutation of cyclohexanone ($3C_6H_{10} \rightleftharpoons 2C_6H_{11}OH + C_6H_5OH$), which occurs on various metallic and oxide catalysts [27, 28], it also occurs on a pure charcoal catalyst, as our direct experiments showed. Like previous investigators, we assume that the reaction involves cylcohexanone molecules in the enol form, the content of which is > 50% in the liquid phase and close to 100% in the vapor, according to the latest data [29]. In this case, for the dismutation there will actually be the same reaction scheme as was adopted for cyclohexene and, consequently, the same value of E° as it is as yet impossible to evaluate the effect of the OH group on the energy of the C−C bond of the ring.

It was then necessary to make thermodynamic calculations on the reactions examined. The lack of the necessary tabular data made it impossible to calculate the equilibrium constants for all the reactions listed in Table 1. In the cases where the calculation was possible, we made only a first or zero approximation as it was impossible to assess accurately the mean error of all the starting data and the calculation as a whole; in any case, the error for ΔH and ΔS for a number of reactions was not less than a few kcal/mole (or cal/mole · deg), while for ΔC_p it did not exceed 6 cal. For cyclohexanol, the conversion to the vapor state was made by calculation of $\Delta H_{ev}^{25^{\circ}}$ by appropriate methods [30, 31], starting from

TABLE 2

Data of Thermodynamic Calculations

No.	Reaction	Degree of approximation	K_p		
			300°	400°	500°
1	Dehydrogenation of cyclohexanol	1	9,33	$5,47 \cdot 10^{1}$	$2,04 \cdot 10^{2}$
2	Dehydration of cyclohexanol	1	$2,72 \cdot 10^{4}$	$1,40 \cdot 10^{5}$	$4,75 \cdot 10^{5}$
3	Irreversible catalysis of cyclohexene	1	$3,06 \cdot 10^{1}$	$1,94 \cdot 10^{7}$	$2,31 \cdot 10^{6}$
4	Dismutation of cyclohexanone (according to data in [36])	2	$4,51 \cdot 10^{1}$	$2,04 \cdot 10^{2}$	$1,43 \cdot 10^{1}$
5	Reduction of cyclohexanol to cyclohexane with hydrogen	1	$1,11 \cdot 10^{6}$	$3,92 \cdot 10^{4}$	$3,32 \cdot 10^{4}$
6	Reduction of cyclohexanol by charcoal with the liberation of CO_2	0	$2,4 \cdot 10^{13}$	—	$7,1 \cdot 10^{12}$
7	The same with the liberation of CO	0	$3,7 \cdot 10^{2}$	—	$2,9 \cdot 10^{4}$
8	Hydrogenolysis of C—C bond in cyclohexane	1	$1,02 \cdot 10^{-2}$	$9,52 \cdot 10^{-3}$	$9,03 \cdot 10^{-3}$
9	Hydrogenolysis of C—C bond in cyclohexanol with hexanol-1 formed	1	4,29	1,39	$8,98 \cdot 10^{-1}$
10	Hydrogenation of cyclohexene	1	$1,25 \cdot 10^{3}$	$3,4 \cdot 10^{1}$	2,31
11	Formation of biphenyl:				
	a) from two benzene molecules	1	$1,65 \cdot 10^{-4}$	$2,05 \cdot 10^{-4}$	$2,40 \cdot 10^{-4}$
	b) $2C_6H_5OH_{(g)} + C_{(s)} \rightleftarrows$ $\rightleftarrows C_6H_5 \cdot C_6H_{5(g)} + H_2O_{(g)} + CO_{(g)}$	0	$7,2 \cdot 10^{4}$	—	$4,0 \cdot 10^{4}$
	c) $4C_6H_5OH_{(g)} + C_{(s)} \rightleftarrows 2C_6H_5 \cdot C_6H_{5(g)} +$ $+ 2H_2O_{(g)} + CO_{2(g)}$	0	$9,5 \cdot 10^{15}$	—	$2,6 \cdot 10^{12}$
	d) $2C_6H_5OH_{(g)} + C_{(s)} \rightleftarrows C_6H_5 \cdot C_6H_{5(g)} +$ $+ H_2O_{(g)} + CO_{(g)}$	0	$7,2 \cdot 10^{4}$	—	$4,0 \cdot 10^{4}$
	e) $C_6H_{6(g)} + C_6H_5OH_{(g)} \rightleftarrows C_6H_5 \cdot C_6H_{5(g)} +$ $+ H_2O_{(g)}$	0	$1,6 \cdot 10^{3}$	—	$3,3 \cdot 10^{1}$
	f) $2C_6H_{6(g)} + CO_{2(g)} \rightleftarrows C_6H_5 \cdot C_6H_{5(g)} +$ $+ H_2O_{(g)} + CO_{(g)}$	1	$1,5 \cdot 10^{-5}$	—	$1,4 \cdot 10^{-4}$
	g) $2C_6H_{6(g)} + CO_{(g)} \rightleftarrows C_6H_5 \cdot C_6H_{5(g)} +$ $+ H_2O_{(g)} + C_{(s)}$	1	$3,3 \cdot 10^{1}$	—	$2,4 \cdot 10^{-2}$

the value $\Delta H_{ev}^{161^\circ} = 10.9$ kcal/mole [32] and the critical point of 377° [33]. The entropy correction was calculated from the equation $\Delta S = \frac{\Delta H_{ev}^{25^\circ}}{T} + R \ln \frac{p_1}{p_2}$, where $p_2 = 760$ mm and $p_1^{25^\circ} = 1.7$ mm [34]. For cyclohexanone, ΔH^{25° form (g) was found from the heat of combustion*, neglecting a temperature difference of 5°, and S (g) $^{25^\circ}$ was calculated from data in [35, 36]. $\Delta H_{form\ (g)}^{25^\circ}$ of phenol was estimated approximately. The other values for the calculations were taken from handbooks [37, 38].

If the equilibrium yields of the initial main and parallel directions of cyclohexanol conversion were calculated, i.e., the equilibrium concentration of cyclohexene x and cyclohexanone y were determined both for when pure cyclohexanol was introduced into the reaction and when it was passed in a stream of N_2 or H_2 in amounts of 1.6 mole per mole of alcohol, then it was found that at 400° and 1 atm x was approximately 200 times greater than y in the first and second cases and approximately 40,000 times greater in the third case (excess H_2).

*Determined by S.M. Shtekher (Moscow State University).

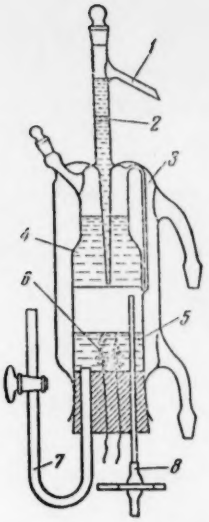


Fig. 2. Electrolytic burette: 1) outlet to reactor; 2) valve consisting of a glass filter with a drop of mercury on it (there is no need for the valve if there are no pressure drops in the system); 3) thermostatting jacket; 4) substance introduced; 5) 20% alkali solution; 6) Pt or Ni electrodes; 7) tube for draining alkali; 8) tube for rapid discharge of oxygen-hydrogen mixture and stopping input.

Considering all the above calculations (Tables 1 and 2) and the previously established fact that hydrogen does not add to cyclohexene in the presence of charcoal [1], one would expect to find that the conversion products of cyclohexanol would contain considerable amounts of cyclohexene, smaller amounts of cyclohexanone and cyclohexane, and even smaller amounts of benzene, phenol*, and ethers, assuming that the latter are formed at all. Carrying out the reaction in excess hydrogen should lead to a fall in the amount of cyclohexanone (and possibly phenol), a fall in the amount of benzene or possibly its complete absence, and a certain increase in the amount of cyclohexane. With an increase in temperature, the cyclohexene yield should increase appreciably and the phenol yield should also increase, but to a lesser extent, while in experiments with excess hydrogen, one can expect definitely only an increase in the amount of cyclohexane and cyclohexene.

EXPERIMENTAL**

The work was carried out in a normal apparatus of the flow type with a quartz tube (16 mm). The furnace temperature was maintained with an accuracy of ± 1° and electrolytic H_2 and N_2 [39] were carefully freed from oxygen and dried. After being shaken with activated charcoal, the cyclohexanol was distilled at 160.5° (758.5 mm) and f.p. 23-24° and n_D^{26} 1.4638; it was introduced into the furnace with a somewhat modified Vasserberg electrolytic burette [40] (Fig. 2) at a constant temperature of 30°. The activated charcoal, which was prepared from chemically pure sucrose by heating in a muffle furnace with subsequent activation in a CO_2 stream in a rotating furnace for 6 hr at 800-850° to 40-45% burn-up, had an ash content of 0.01-0.03%, a packed specific gravity of 0.30 g/cc, a one-hour activity with ether of 10% and a one-day activity of 42%, a surface of 185-200 m^2/g from adsorption of I_2 from solution, a surface of 332 m^2/g from the adsorption of n-heptane (determined by E.P. Maksimova by a gravimetric method with evaculation at 400°); after the experiments the surface of the charcoal had been reduced somewhat: to 141-147 m^2/g (from I_2) and 300 m^2/g (from p-C_5H_{12})***. Due to the fact that the activity of the charcoal fell considerably during the experiments, in order to obtain reproducible results we passed a strictly constant amount of cyclohexanol over the catalyst each time and activated the charcoal before each experiment by passing the same portion of water vapor twice and flushing with N_2 before and after for 2 hr at 450°. Observations in [41-43] established that there is no oxidation during the treatment of charcoal with water to restore its surface.

The emergent gases were analyzed on a VTI apparatus only in experiments with pure cyclohexanol. The liquid catalyzate was weighed before and after removal of the water layer and dried with anhydrous Na_2SO_4 and two parallel samples used for the determination of cyclohexanone (oxime titration [44]) and cyclohexene (bromometrically [45]); the accuracy of the analysis on artificial mixtures was ± 1%. In separate cases, the anhydrous catalyzates from several identical experiments were combined and the Raman spectra determined. Phenol and

*The formation of phenol, a dismutation product, is impeded by the second dismutation product, cyclohexanol, which continuously enters the system.

**With the assistance of E.P. Filippova (Mikos).

***The work was carried out with three portions of charcoal, which were similar in constants. One series of experiments, whose results are given in Table 5, was carried out on birchwood activated charcoal with an ash content of 0.41% and a one-day activity with ether of 55.5%.

TABLE 3

Effect of Experimental Conditions on Catalyzate Composition
Amount of charcoal, 2.2 g; experiment duration, 36 min; amount of cyclohexanol introduced, 7.5 g; input rate, 0.2 ml/min (30°); molar ratio $C_6H_{11}OH$: N_2 (or H_2), 1: 1.6

No.	Substance introduced	Temperature in °C	Content in catalyzate [a] in %	
			cyclohexanone	cyclohexene
1	Cyclohexanol [b, c]	400	2,2--3,0	31,2--31,8
2	Cyclohexanol + H_2 [c]	200	0,6	35,0
3	The same	300	0,7	68,0
4	"	400	1,5	67,0
5	"	500	19,3	28,0
6	Cyclchexanol + N_2	200	0,9	12,2
7	The same	300	1,1	47,8
8	"	400	2,7	51,0
9	"	450	11,6	39,3
10	"	500	16,9	25,2

Footnote. [a] Table 3 gives the composition of the catalyzate and not the yield as the latter should be calculated from the equilibrium value, which is practically impossible; the yields in percents of "theoretical" (i.e., 100%) would be close to the percent composition presented in Table 3.

[b] The results given are those of experiments on different samples of charcoal, prepared by the same method. Composition of emergent gases in vol. %: CO ~ 0.5, CO_2 ~0.5, unsaturated hydrocarbons ~1-2, and the remainder, H_2.

[c] Biphenyl appeared in insignificant amounts (a few milligrams in each experiment) beginning at 300° (a rise in temperature hardly affected the amount of biphenyl); it had m.p. 68° after recrystallization from alcohol and a mixed melting point with pure biphenyl was not depressed (69°). The crystals were identified under a polarization microscope. Phenol appeared above 200° and the condensate after activation of the catalyst with steam contained 0.008 weight % of phenol at 200-300°, 0.04 weight % at 400°, and 0.1 weight % at 500°.

TABLE 4

Results of Spectral Analysis

Substances introduced	Experiment temperature in °C	Relative amounts of substances in catalyzate
Cyclohexanol + N_2	400	Cyclohexene, cyclohexanol, cyclohexane, benzene, cyclohexanone
The same	450	Cyclohexene, cyclohexanol, cyclohexanone, cyclohexane, benzene
The same	500	Cyclohexane, cyclohexene, cyclohexanone, benzene, cyclohexanol
Cyclohexanol + H_2	500	Cyclohexene, cyclohexane, cyclohexanone, cyclohexanol, benzene.

biphenyl were strongly held by the charcoal surface and were therefore absent from the catalyzate; they were found in the aqueous condensate, formed during the activation of the catalyst with steam. After separation of the biphenyl, the phenol was determined by titration [44]. Pyrolysis of cyclohexanol began at ~500° in an empty quartz tube. A total of more than 100 experiments were carried out and the results of typical experiments are given in Table 3.

The Raman spectra were plotted on an ISP-51 instrument with a central cell and a linear dispersion of ~30 A/mm in the region of $\lambda \approx 4500$ A. Quantitative results could not be obtained due to the inadequate linear dispersion. However, interpretation of the spectra made it possible to determine the relative amounts of the substances in the catalyzate (they are listed in decreasing order in Table 4).

Frequencies characteristic of an ether bond, acyclic compounds, or a five-membered ring were not detected in the spectra.

TABLE 5

Results of experiments on the Determination of the Temperature Dependence of the Cyclohexane Yield
Amount of charcoal, 11.6 g; input rates for cyclohexanol and H_2, the same as previously

Temperature in °C	Catalyzate composition in % on cyclohexanol passed*		
	cyclohexene	cyclohexane	cyclohexanone
370	4,3	6,2	0
400	23,0	22,7	13,0
400	20,6	22,3	13,2
475	39,2	18,0	13,0

*The amount of the other reaction products was not established.

We then give the results of separate experiments for determining the effect of temperature on the amount of cyclohexane formed (Table 5) and demonstrating that cyclohexanone undergoes dismutation (Table 6).

DISCUSSION OF EXPERIMENTAL RESULTS

As can be seen from a comparison of the experimental data with the theoretical calculation of the sequence of reactions from the values of E", out of the sixteen reactions listed in Table 1, all the first five occurred. These reactions have the lowest absolute values of E" (from 139.3 to 156.3 kcal). None of the reactions with a higher calculated energy barrier, reaching 200 kcal, occurred. The experimental and theoretical reaction sequences coincide as far as may be judged with the complexity of the catalyzate composition and the interrelation between a series of reactions with the exception that cyclohexene always predominated in the products in practice, while the reaction leading to the formation of cyclohexanone has the lowest absolute value of E". However, if we consider what has been said above on the relation between the equilibrium yields of these products (p. 617) and also that part of the cyclohexanone formed is consumed in the dismutation reaction, then there is a simple explanation for this apparent exception.

TABLE 6

Dismutation of Cyclohexanone
Amount of charcoal, 1.6 g; flow rate of pure cyclohexanone, 0.2 ml/min; temperature, 400°

Approximate composition of catalyzate in %					
cyclohexanone	cyclohexanol	phenol	cyclohexene	cyclohexane	benzene
10	50	30	2	5	2

Only the appearance of biphenyl in the products remains not quite clear, though there were only small amounts of it. Its formation by any of the hypothetical mechanisms has an energy barrier which is considerably higher, for example, than the formation of ethers or the hydrogenation of cyclohexene, which did not occur in

our experiments. The value of E" for the formation of biphenyl by codehydration of benzene and phenol, which is not given in Table 1, is only 151.8 kcal if we do not consider the conjugation of benzene rings with the system of double bonds of graphite. However, it would be incorrect to neglect this conjugation as it unavoidably arises and this leads to an increase in the value of E" to 170-180 kcal. Therefore, it is necessary to assume that biphenyl is obtained as a result of charcoal participation in the reaction not as a catalyst, but as a component. This may occur either as a result of charcoal acting as a reducing agent in the reaction of two phenol molecules (oxidized only on the surface) or when the surface oxides of charcoal are oxidizing agents and eliminate hydrogen atoms from two benzene molecules, for example: $2C_6H_6 + CO = C_6H_5 \cdot C_6H_5 + H_2O + C$. In view of the fact that carbon oxides were almost absent from the gaseous reaction products, the latter route to the formation of biphenyl (it is thermodynamically possible according to the calculation in Table 2, in which the change in energy of the surface atoms or groupings was neglected) is most probable.

The very small content of carbon oxides in the gaseous reaction products indicates that the formation of cyclohexane in our experiments was only the result of irreversible catalysis of cyclohexene and reduction of cyclohexanol by hydrogen and not due to reduction of the latter by charcoal, as was reported in the work of Zelinskii and Gaverdovskaya [46]. This contradiction may be explained by the specific characteristics of the charcoal they took, which had an ether activity of 54.5%, and the fact that 40 cm of the catalyst catalyst tube was filled.

In conclusion we will examine the need for considering bond strain in the multiplet complex, which was mentioned above. In the given case, this need arises because the catalyst is charcoal and not a metal (or oxide). Metallic and covalent bonds are different. Metals are characterized by considerable diversity of the valence states and a high density of electron levels. From this it follows that the direction of their bonds with atoms of the reacting molecules will not be strictly fixed in space and consequently there is no need to consider strain. On the other hand, carbon atoms at the lattice points of graphite* have strictly directed bonds. In actual fact, calculation shows that if we do not consider the strain arising in this case, the absolute value of E" is found to be implausibly high. Thus, for example, in the case of cyclohexanol dehydration, which proceeds readily, we obtain E" = - 174.7 kcal (instead of -146.6 kcal when strain is considered), i.e., the energy barrier is as high as that for the codehydrogenation of two cyclohexane molecules to bicyclohexyl, which does not occur up to at least 500°.

The direction of the valence bonds of carbon atoms of the catalyst with atoms of the reacting molecules and their much more covalent character may also provide the second possible explanation for the fact that the calculated values of E" are so great. We should remember that in our calculation it is assumed that there is complete rupture of the bonds at the moment of reaction and the calculation does not refer to the saddle point of the potential surface, as should have been the case. However, the agreement between the calculated reaction sequence and that observed experimentally shows that the two series of values are symbatic.

We would like to thank P.P. Shorygin and I.P. Yakovleva for plotting the spectra and help in interpreting them.

SUMMARY

1. The products from the conversion of cyclohexanol over activated charcoal in a stream of H_2 and N_2 at 200-500° are cyclohexene, cyclohexanone, cyclohexane, benzene, phenol, and biphenyl.

2. The equations of the multiplet theory were used for calculating the energy barriers of the corresponding reactions and their theoretical sequence was found. It was shown that it is necessary to consider the bond strain in the multiplet complex for the case of a charcoal catalyst.

3. Thermodynamic calculations were made for the equilibria of a series of reactions in the first and zero approximations.

4. It was established that cyclohexanone undergoes dismutation on pure charcoal, beginning at 200°.

5. The experimental results are in agreement with the sequence of cyclohexanol conversions calculated from the multiplet theory with allowance for thermodynamic limitations.

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PROPERTIES AND STRUCTURE OF $NiO - Al_2O_3$ CATALYSTS

COMMUNICATION 4. X-RAY AND MAGNETOCHEMICAL INVESTIGATIONS OF THE FORMATION OF A SPINEL FROM COPRECIPITATED NICKEL AND ALUMINUM HYDROXIDES

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In our previous papers [1-3] on the investigation of $NiO-Al_2O_3$ catalysts obtained by coprecipitation of nickel and aluminum hydroxides followed by firing of the hydroxides, we showed that with an NiO concentration from 0 to 50 mol. % and firing temperatures of 400° and above, these catalysts formed a monophase system with a cubic, face-centered lattice of a spinel type. The purpose of the present article was an investigation of the process and conditions for the formation of a spinel structure from coprecipitated nickel and aluminum hydroxides and its ordering during thermal treatment.

EXPERIMENTAL

The starting hydroxide mixture was precipiatated at 20° with a small excess of 10% NH_4OH from a solution containing aluminum and nickel nitrates in a molar ratio of 2:1 (or converted to Al_2O_3 and NiO, 1:1). The precipitate was carefully washed by decantation and dried in a drying cupboard for 6 hours at 100°. Separate portions of the dried precipitate were heated in a crucible furnace for 6 hours at 150-1200° (see Table 1), after which they were investigated and analyzed.

The water content was determined by the loss in weight after firing of the sample at 1200°. The ratio Ni : : Al_2O_3 was calculated from analytical data on the nickel content of the samples. The analytical results are given in Table 1.

Two methods were used for the investigation of the samples: x-ray and magnetic. The procedure for x-ray and magnetic investigations was described in our previous articles [1-3]. The x-ray measurement results are given in Table 2 and the magnetic measurement results in Table 3.

DISCUSSION OF EXPERIMENTAL RESULTS

In examining the interplanar distances d and line intensities I, given in Table 2, we should first note that the diffraction picture presented by the samples fired at 100 to 250° is not characteristic of either aluminum hydroxide or nickelous hydroxide, nor is it an additive diffraction picture of a mixture of them. This phenomenon indicated that the substance we had was either a mixed hydroxide of nickel and aluminum or a solid solution of these hydroxides. The work of other authors confirms this conclusion. For example, when using alkali precipitation, the French investigator, Longuet-Escard [4] obtained nickel hydroaluminate, while Chalyi and Rozhenko [5] obtained a solution of $Ni(OH)_2$ in hydrargillite. When x-ray data are compared with those of the above

TABLE 1

Sample Composition

Portion No.	Firing temperature in °C	Sample composition in wt. %			Composition in mole fractions
		NiO	Al_2O_3	H_2O	
1	100	23,7	32,7	43,6	$NiO \cdot Al_2O_3 \cdot 7,6\ H_2O$
2	150	26,2	36,0	37,8	$NiO \cdot Al_2O_3 \cdot 6,0\ H_2O$
3	200	29,0	40,0	31,0	$NiO \cdot Al_2O_3 \cdot 4,4\ H_2O$
4	250	37,0	51,1	11,9	$NiO \cdot Al_2O_3 \cdot 1,3\ H_2O$
5	300	36,9	50,9	12,2	$NiO \cdot Al_2O_3 \cdot 1,4\ H_2O$
6	350	38,9	53,6	7,5	$NiO \cdot Al_2O_3 \cdot 0,8\ H_2O$
7	400	40,4	55,6	4,0	$NiO \cdot Al_2O_3 \cdot 0,4\ H_2O$
8	450	40,4	55,7	3,9	$NiO \cdot Al_2O_3 \cdot 0,4\ H_2O$
9	500	40,4	55,8	3,8	$NiO \cdot Al_2O_3 \cdot 0,4\ H_2O$
10	700	41,2	56,9	1,9	$NiO \cdot Al_2O_3 \cdot 0,2\ H_2O$
11	800	41,4	57,1	1,5	$NiO \cdot Al_2O_3 \cdot 0,15\ H_2O$
12	900	41,7	57,4	0,9	$NiO \cdot Al_2O_3 \cdot 0,1\ H_2O$
13	1200	42,0	58,0	0	$NiO \cdot Al_2O_3$

authors it is noticeable that the chemical nature of the precipitant and the precipitation conditions greatly affect the structure of the mixed hydroxide (or, according to Longuet-Escard, the nickel hydroaluminate) as in all three cases the x-ray obtained is different.

The magnetic susceptibility calculated per g of nickel falls sharply over the temperature range examined (Fig. 1). Such a change in susceptibility is related to the sharp change in the Weiss constant Δ which changes sign at 200° and has a maximum at 300° (Fig. 2).

As is known, $\Delta = \frac{-2Iz\underline{S}(S+1)}{3k}$, where I is the exchange integral, $\underline{z}$ is the number of adjacent, equidistant paramagnetic ions (paramagnetic environment), and S is the vector sum of spin moments. From this formula it follows that Δ may change as a result of a change in the exchange interaction I or a change in the parmagnetic environment $\underline{z}$. A change in the exchange interaction should have produced a decrease in the magnetic moment μ, but, as Fig. 2 shows, the value μ remained constant at all firing temperatures and equal to $2.9 \pm 0.1\ \mu V$, which is characteristic of Ni^{2+}. It is thus clear that the change in Δ is connected solely with the change in the paramagnetic environment of Ni^{2+} ions, and this occurs as a result of gel decomposition and crystal formation. Actually, Fig. 1 shows that at 100-250° the removal of most of the water from the samples is accompanied by a sharp change in magnetic susceptibility.

The temperature range 250-300° is a transitional one from the structural point of view. It is in this range that the crystal lattice is rearranged. A sample at 300° gives an x-ray diffraction picture that is completely different from the one for samples fired at a lower temperature. The new diffraction picture is identical with that of γ-Al_2O_3, which has a defective spinel structure; the only difference is that higher values were obtained for $\underline{d}$ than in the case of γ-Al_2O_3 and this confirms the presence of spinel in the sample.*

The rearrangement of the crystal lattice is accompanied by a change in the character of Ni^{2+} ion interactions, as is shown by the change in the sign of the Weiss constant, the sharp increase in its absolute value and attainment of a maximum at 300°. These changes in the Weiss constant agree with the change in the x-ray picture in this temperature range. Two processes occur in the temperature range from 300 to 1200°. Firstly, the spinel crystal lattice is ordered and completed. This is illustrated by the x-ray diffraction lines which become

* The higher values of $\underline{d}$ in the spinel $NiAl_2O_4$ as compared to those of γ-Al_2O_3 are explained by the fact that, with a similar lattice symmetry, the number of cations in $NiAl_2O_4$ per elementary cell is greater than in γ-Al_2O_3. In addition, the Ni^{2+} ions are larger than Al^{3+} ions (their radii are 0.74 and 0.57 A, respectively).

TABLE 2

Interplanar Distances d in A and Relative Intensities I of Diffraction Lines

Solid solution of nickel and aluminum hydroxides or nickel hydroaluminate								Spinel $NiAl_2O_4$																		Refractive indices of spinel
100°		150°		200°		250°		300°		350°		400°		450°		500°		700°		800°		900°		1200°		
I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	
						ср	4,7																				
ср	4,3	ср	4,4	ср	4,4																					
						ср	4,1																				
осл.	$3,6_5$	осл	3,6	сл	3,6	сл	3,5																			
оосл	2,90	осл	2,95	осл	3,00	оосл	2,83									оосл	2,80	осл	2,85	оосл	2,85	осл	2,85	срсл	2,82	(022)
осл	2,50	сл	2,48	сл	2,52	срсл	2,45	срсл	2,43	ср	2,40	ср	2,41	яср	2,40	я	2,41	ср	2,41	срсл	2,41	яср	2,41	оя	2,41	(113)
		осл	2,22																							
осл	2,01	оосл	2,09	осл	1,96	ср	2,03	ср	2,01	я	2,01	я	2,02	я	2,02	оя	2,01	я	2,02	яср	2,01	я	2,00	я	2,00	(004)
		оосл	1,87																							
		оосл	1,73																							
оосл	1,62	оосл	1,60	сл	1,50	оосл	1,57									осл	1,55	осл	1,56	оосл	1,56	осл	1,55	ср	1,54	(333)
сл	1,46	срсл	1,46	сл	1,45	ср	1,43	ср	1,43	я	1,42	яср	1,42	я	1,42	оя	1,42	я	1,42	я	1,42	оя	1,42	оя	1,42	(044)
																								осл	1,36	(135)
																								осл	1,27	(026)
																				оосл	1,220	осл	1,220	срсл	1,220	(335)
																								ср	1,158	(444)

Note: ср – average; осл – very weak; оосл – very very weak; сл – weak; срсл – average weak; я – bright; яср – bright average; оя – very bright.

TABLE 3

Magnetic Susceptibility of Samples, Calculated per g of Sample (χ_{sam}) and per g of Nickel (χ_{Ni})

Firing temperature in °C	$\chi_{sam} \cdot 10^6$			$\chi_{Ni} \cdot 10^6$		
	20°	80°	160°	20°	80°	160°
100	15,0	11,6	—	82,7	61,8	—
150	16,3	13,0	—	81,0	65,1	—
200	17,3	13,7	11,2	77,3	61,4	50,5
250	17,0	13,6	11,6	59,3	47,6	40,7
300	15,1	12,8	11,0	53,0	45,0	38,8
350	15,5	13,4	11,6	51,4	44,5	38,6
400	15,3	12,9	11,0	49,0	41,5	35,4
450	15,6	13,1	11,4	49,8	42,0	36,7
500	16,0	13,5	11,3	51,0	43,3	36,4
700	16,5	13,9	11,4	51,5	43,5	35,8
800	16,9	13,9	11,6	52,5	43,4	36,2
900	18,5	15,1	12,7	57,1	46,7	39,4
1200	21,3	17,0	13,8	65,0	52,0	42,3

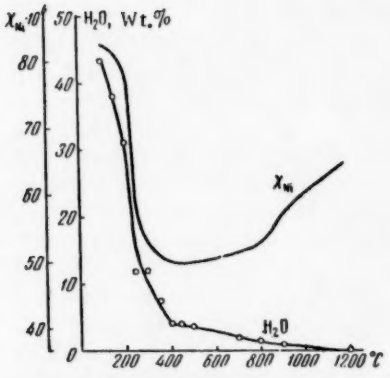

Fig. 1. Change in the magnetic susceptibility of samples at room temperature (calculated per g of Ni) in relation to firing temperature. The curve for the change in the water content of samples is given for comparison.

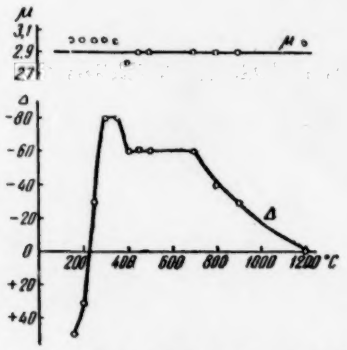

Fig. 2. Change in Weiss constant Δ and magnetic moment μ in relation to firing temperature.

more intense and sharp with an increase in temperature, a change which is also due to the growth of the primary crystals from the thermal treatment, and the number of lines also increases. Secondly, there is a further decrease in the water content of the samples, to 0.4 at 400-500°, 0.2 at 700°, 0.1 at 900°, and 0 at 1200° (in mole fractions).

As Figs. 1 and 2 show, the magnetic susceptibility hardly changed over the range 300-700° and Δ remained constant. This, apparently, is due to the fact that a spinel type of crystal structure is mainly formed by 300° and with a further increase in temperature and decrease in water content there is only ordering of this structure which does not involve the rearrangement of Ni^{2+} ions relative to each other. With an increase in firing temperature above 700° the magnetic susceptibility starts to increase appreciably, while the absolute value of Δ to decrease. Apparently, in the range 700-1200°, besides the general ordering of the crystalline lattice, there is also redistribution of Ni^{2+} ions between the octahedral and tetrahedral spaces, which results in the formation of reverse spinel. According to literature data the reversibility coefficient of spinel $NiAl_2O_4$ reaches a considerable value: according to Romejn [6], it is 0.76 and according to the data in [7], 0.69-0.81. The total effect of such a redistribution of Ni^{2+} ions apparently results in a decrease in the paramagnetic environment z, which induces a fall in the absolute value of Δ and, consequently, an increase in the magnetic susceptibility in the range 700-1200°.

SUMMARY

It was shown by x-ray and magnetochemical methods that the formation of spinel from coprecipitated nickel and aluminum hydroxides by thermal treatment consists of the following stages: a) formation of a solid solution of nickel and aluminum hydroxides or nickel hydroaluminate by coprecipitation; b) decomposition of the gel and crystal formation in the range 100-250°, accompanied by a sharp decrease in the water content; c) rearrangement of the crystal lattice at 250-300° to a cubic, face-centered spinel-type lattice; d) ordering of the crystal lattice at 300-700° without noticeable redistribution of Ni^{2+} ions, accompanied by a gradual decrease in water content; and e) further ordering of the crystal lattice at 700-1200° with redistribution of Ni^{2+} ions in accordance with the reversibility coefficient of spinel $NiAl_2O_4$.

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PARTICIPATION OF SOLVENT IN THE ACTIVATED COMPLEX OF MENSHUTKIN REACTIONS

COMMUNICATION 2. ESTIMATION OF THE SOLVATION OF THE ACTIVATED COMPLEX IN THE REACTION OF PYRIDINE WITH ETHYL IODIDE IN ETHANOL AND IN ACETONE

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In a previous communication [2] we presented the results of an investigation of the kinetics of the reaction of pyridine with ethyl iodide in ethanol at 50° and pressures up to 2000 kg/cm². Data on the effect of pressure on the rate of the same reaction in acetone at 40°, which was obtained by one of us and Zhulin [2], was published previously. In the present investigation we measured the change in volume during the reaction of pyridine with ethyl iodide in the two solvents mentioned and also the electrical conducivity of solutions of the reaction product, N-ethylpyridinium iodide. From a comparison of the data obtained with the results of [1, 2], an approximate estimate was made of the degree of solvation of the activated complex in the reaction studied.

Let us write the over-all scheme for the reaction in the liquid phase in the absence and presence of solvent:

$$\begin{array}{ccccccc} C_5H_5N+C_2H_5I & \xrightarrow{\Delta_1V^{\neq}} & C_5H_5N\ldots C_2H_5I & \longrightarrow & C_5H_5\overset{+}{N}C_2H_5I^- \\ \Delta V_0 \downarrow & & \Delta_2V^{\neq} \downarrow & & \Delta V_s \downarrow \\ (C_5H_5N+C_2H_5I)_s & \xrightarrow{\Delta V^{\neq}} & (C_5H_5N\ldots C_2H_5I)_s & \longrightarrow & \left[\begin{array}{c} C_5H_5\overset{+}{N}C_2H_5I^- \\ \updownarrow \\ C_5H_5\overset{+}{N}C_2H_5+I^- \end{array}\right]_s \end{array} \qquad (1)$$

Here the index s denotes that the substance is in solution; ΔV_0 is the change in volume during solutions of the reacting substances; $\Delta_1V^{\neq}$ is the change in volume during the formation of one mole of activated complex from the starting materials in the absence of solvent; $\Delta_2V^{\neq}$ is the volume effect of solvation of the activated complex; and $\Delta V_s^{\neq}$ is the volume effect of solvation of the reaction product. The value of $\Delta V^{\neq}$, which is the change in volume during the formation of one mole of activated complex in the presence of solvent, may be determined from data on the pressure dependence of the rate constant [3]. According to (1)

$$\Delta V = \Delta_1V^{\neq} + \Delta_2V^{\neq} - \Delta V_0 . \qquad (2)$$

As the present investigation showed, the solution of pyridine and ethyl iodide in ethanol is accompanied by hardly any change in volume. Consequently, in the given case

$$\Delta V^{\neq} = \Delta_1V^{\neq} + \Delta_2V^{\neq}. \qquad (3)$$

According to formula (3), for determining the value of $\Delta_2V^{\neq}$ it is necessary to find the value of $\Delta V^{\neq}$ from experimental data on the pressure dependence of the reaction rate constant and also to estimate the value of $\Delta_1V^{\neq}$.

Gonikberg and Povkh [4] estimated the value of $\Delta_1 V^{\neq}$ for the reaction of pyridine with ethyl iodide by taking the molar volume of the liquid reaction product as equal to the molar volume of the unsolvated activated complex. On the basis of a model of the activated complex in Menshutkin reactions [6], Gonikberg and Kitaigorodskii [5] recently calculated the contraction during the formation of the activated complex from data on intermolecular radii and bonds lengths. Calculation by the first of the methods mentioned [4] gives for the reaction of pyridine with ethyl iodide a value of $\Delta_1 V^{\neq}$ of -22.5 cc/mole at 50°, -20.5 cc/mole at 30°, and -17.5 cc/mole at 0°. The value of $\Delta_1 V^{\neq}$ for the same reaction, calculated by the second method [5], equals -14 cc/mole regardless of the temperature as this calculation allows for only the contraction caused by overlapping of the spheres described by the intermolecular radii. However, in [5] no allowance was made for additional contraction between the hydrogen atoms and the methyl groups in the alkyl halide, on the one hand, and the halogen atom, on the other, arising during the formation of the activated complex. According to the calculation of Kitaigorodskii, the magnitude of this contraction in alkyl iodides is 2.6 cc/mole for one methyl group and 0.8 cc/mole for one hydrogen atom. Thus, for the reaction of pyridine with ethyl iodide, the value of $\Delta_1 V^{\neq}$ calculated from the model of the activated complex is not -14 cc/mole, but -18 cc/mole. However, it can be shown that the negative values of $\Delta_1 V^{\neq}$ obtained by calculation from the intermolecular radii and bond lengths are actually somewhat low. Experimental data available in the literature on the effect of pressure on the rate of additions in the absence of solvent (see [7]) indicate that there is a considerable decrease in the negative value of $\Delta V^{\neq}$ (equal to $\Delta_1 V^{\neq}$ in this case) with an increase in pressure from atmospheric to one or two thousand atmospheres. This decrease in $\Delta V^{\neq}$ cannot be caused solely by a decrease in the intermolecular radii as the pressures are too low for this. Therefore, it might be expected that the observed effect is caused to a certain extent by the change in free volume*.

If we denoted the change in free volume during the formation of the activated complex by ΔV_{free}, then on the basis of what has been presented, we may write for addition reactions

$$\left(\frac{\partial \Delta V_{free}}{\partial P}\right)_T > 0. \tag{4}$$

On the one hand, as the pressure increases

$$\Delta V_{free} \to 0. \tag{5}$$

From (4) and (5) it follows that in addition reactions

$$\Delta V_{free} < 0. \tag{6}$$

Consequently, the true value of $\Delta_1 V^{\neq}$ in the reaction studied apparently has a more negative value than -18 cc/mole.

An investigation of the kinetics of the reaction in ethanol [1] made it possible to find the change in the volume of the system ($\Delta V^{\neq}$) accompanying the formation of the activated complex at 50° and atmospheric pressure: $\Delta V^{\neq} = 27.8$ cc/mole. According to data in [2], in the reaction in acetone (40°, p = 1 atm), $\Delta V^{\neq} = -34$ cc/mole**. If it is assumed in accordance with data in [4] that the value of $\Delta_1 V^{\neq}$, i.e., the change in volume during the formation of the unsolvated activated complex at 50° and atmospheric pressure, equals -22.5 cc/mole, then from formula (3) the value of $\Delta_2 V^{\neq}$, i.e., the change in volume as a result of solvation of the activated complex, equals -5.3 cc/mole. For acetone at 40° and atmospheric pressure, $\Delta_2 V^{\neq} = -12$ cc/mole.

The comparison of the values of $\Delta_2 V^{\neq}$ with the volume effect of solvation of ions of the reaction product made in the present work and also some calculations based on the experimental data obtained make it possible

*By free volume we mean the difference between the volume of the liquid substance, on the one hand, and the volume of molecules contained in it with "envelopes" described by intermolecular radii, on the other.

**Corrected to allow for the compressibility of the solvent in accordance with equation (1) in [1].

Fig. 1. Equivalent electrical conductivity of N-ethylpyridinium iodide solutions in ethanol (at 50°) (1) and in acetone (at 40°) (2).

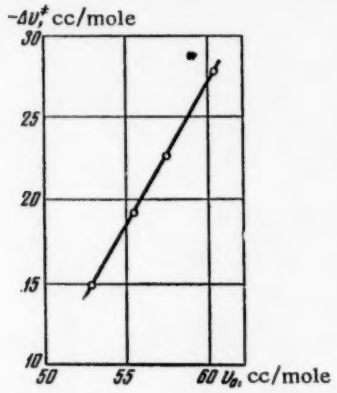

Fig. 2. Relation of $\Delta V^{\neq}$ to the volume of the solvent (ethanol) at 50° and pressures up to 2000 kg/cm^2.

to draw the conclusion that the activated complex in the reaction studied is solvated to a considerably lesser extent than iodine and N-ethylpyridinium ions. This conclusion is in complete agreement with the results of [2] and contradicts the statements in [8, 9] that the activated complex in Menshutkin reactions is solvated almost the same as ions of the reaction product.

In the present work we attempted to take the next step toward a quantitative estimation of the degree of solvation of the activated complex. This approximate estimation was found to be possible only if certain assumptions formulated below are made. In general, the different approaches to the solution of this problem we adopted led to results which agreed.

EXPERIMENTAL

To compare the solvation of the activated complex and ions of the reaction product, we measured the change in volume of the system ΔV during the formation of one mole of reaction product at atmospheric pressure and determined its degree of dissociation in ethanol and in acetone at various concentrations. ΔV was determined by direct measurement of the solution density in a pycnometer of 60 ml capacity. Flasks containing 100 ml each of 1 M solutions of C_5H_5N and C_2H_5I* in absolute ethanol were placed in a thermostat; the solutions were mixed rapidly when they had heated to 50°. The solution obtained was used to fill a pycnometer in a thermostat (temperature of 50 ± 0.02°); the remainder of the solution was rapidly cooled to 20° and the C_5H_5N in it determined by the procedure described previously [1]. After the density had been determined, the solution was poured from the pycnometer and the C_5H_5N in it also determined (at 20°). The initial concentration of C_5H_5N in the solution, which equaled ~0.5 M, was taken as equal to the mean of the two values obtained. The solution was then returned to the thermostat and, as the reaction proceeded, we periodically determined the solution density and the C_5H_5N concentration before and after determination of the density. ΔV was calculated from the formula

$$-\Delta V = \frac{1000\,(d_x - d_0)}{x d_0}, \qquad (7)$$

where d_0 and d_x are the solution densities before the reaction and at a concentration of reaction product of x, respectively (at 50°). Only two experiments were carried out with alcohol solutions. The accuracy of the determination of ΔV was ± 1 cc/mole. These determinations gave the following results.

x, mole/liter	0.1513	0.1842
$-\Delta V$, cc/mole	40	39

The results we obtained analogously by measuring ΔV for the same reaction in acetone at 40 ± 0.02° with initial C_5H_5N and C_2H_5I concentrations of 0.25 M are given below:

x, mole/liter	0.0646	0.0916
$-\Delta V$, cc/mole	63	63**

*The constants of the ethanol, acetone, pyridine, and ethyl iodide used were presented in the previous communication [1]. The N-ethylpyridinium iodide had m.p. 90°.

**The value of ΔV in acetone at the same concentrations and 20° was measured in [2]; it was found to equal 56-57 cc/mole. Thus, the change in ΔV in acetone with an increase in temperature is small.

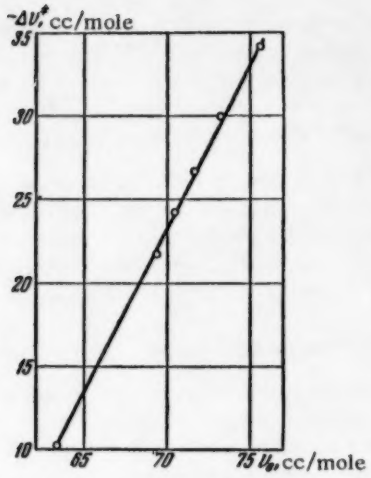

Fig. 3. Relation of $\Delta V^{\neq}$ to the volume of the solvent (acetone) at 40° and pressures up to 3000 kg/cm² (according to data in [2]).

We also found that the volume effect caused by the solution of pyridine and the ethyl iodide in ethanol is less than 1 cc per mole at 20° and concentrations of 0.5 M, which lies within the limits of error of the measurements. The values of the degree of dissociation α, which we needed for subsequent calculations, were determined by measuring the electrical conductivity of solutions of N-ethylpyridinium iodide of various concentrations in absolute ethanol at 50 ± 0.1° and in acetone at 40 ± 0.1°. The electrical conductivity was measured on a Kohlrausch bridge with an 1100 cps ac generator. Data on the relation between the equivalent electrical conductivity and the concentration of N-ethylpyridinium iodide $\underline{x}$ are given in the table. For determining the equivalent electrical conductivity at infinite dilution (λ_∞), the value of λ was plotted on a graph against $\sqrt{x}$ (Fig. 1). The values of (λ_∞) in alcohol and acetone obtained are also given in the table.

The results of an approximate calculation of the degree of dissociation α from the formula

$$\alpha = \frac{\lambda}{\lambda_\infty} \qquad (8)$$

led to the conclusion that the degree of dissociation was small at the N-ethylpyridinium iodide concentrations used in the determination of ΔV:

In ethanol $\underline{x}$ mole/liter	0.1513	0.1842
α	0.19	0.18
In acetone $\underline{x}$ mole/liter	0.0646	0.0916
α	0.22	0.20

DISCUSSION OF EXPERIMENTAL RESULTS

Let us compare the values of $\Delta_2 V^{\neq}$ at atmospheric pressure in alcohol and acetone with ΔV_s, the change in volume caused by solvation of the reaction product. The latter value may be estimated with sufficient accuracy by calculating the contraction during the formation of liquid N-ethylpyridinium iodide [4] from the values of ΔV, i.e., the decrease in volume during the reaction in solution, which we found in the work* . This calculation leads to the following values of ΔV_s:

In alcohol at 50°: $\Delta V_s = -39$ cc/mole - (-22.5 cc/mole) = - 16.5 cc/mole.
In acetone at 40°: $\Delta V_s = -63$ cc/mole - (-22 cc/mole) = - 41 cc/mole.

Our measurements on the electrical conductivity of N-ethylpyridinium iodide solutions in alcohol and acetone showed that, at those concentrations of this compound at which ΔV was determined, its degree of dissociation was very small (0.18 and 0.21, respectively). Had N-ethylpyridinium iodide in the undissociated state been solvated to the same degree as the activated complex, then this this would have meant that, with its complete dissociation, the decrease in volume as a result of solvation of the ions ($-\Delta V_i$) would have been 66 cc/mole in alcohol and 154 cc/mole in acetone. In actual fact it can be assumed that the solvation of undissociated N-ethylpyridinium iodide is greater than the solvation of the activated complex and the values of ($-\Delta V_i$) given above are greater than the true ones. The lower limit for the absolute values of ΔV_i may be found if it is assumed that the formation of solvated ions from the N-ethylpyridinium iodide present in solution is not accompanied by a decrease in volume; then $\Delta V_i = \Delta V_s$. However, it is evident that in actual fact the solvation of the ions is greater than the solvation of the undissociated reaction product. Thus, in alcohol solution:

$$66 \text{ cc/mole} > -\Delta V_i > 16.5 \text{ cc/mole},$$

* In this case we neglect the slight increase in volume caused by the separation of unsolvated iodide and N-ethylpyridinium ions.

TABLE

Equivalent Electrical Conductivity of N-Ethylpyridinium Iodide Solutions

Ethanol (50°)				Acetone (40°)			
Experiment 1		Experiment 2		Experiment 3		Experiment 4	
mole/liter*	λ	mole/liter*	λ	mole/liter*	λ	mole/liter*	λ
0,000944	74,3	0,0000948	107	0,000943	185	0,0000943	238
0,00236	63,8	0,000948	76,1	0,00236	159	0,000956	186
0,00957	48,7	0,00961	50,1	0,00956	115	0,00970	118
0,0239	38,8	0,0975	28,5	0,0239	88,4	0,0984	57,9
0,0971	28,4			0,0970	56,2		
0,243	24,6			0,243	40,2		
	$\lambda_\infty = 140$				$\lambda_\infty = 280$		

* At 20°.

and in acetone solution:

$$154 \text{ cc/mole} > -\Delta V_i > 41 \text{ cc/mole}.$$

These values of ΔV_i are several times greater than the values of $\Delta_2 V^{\neq}$ (-5.3 and -12 cc/mole, respectively, in ethanol and acetone), calculated according to the hypotheses in [4]. Even if these values differ from the true ones by a few cc/mole, this cannot alter the conclusion that the activated complex in the reaction studied is solvated much less than ions of the reaction product.

We then attempted to approach the problem from a somewhat different point of view. Let us assume that the activated complex is solvated with n molecules of solvent. then we can write the following equation

$$\Delta V^{\neq} = V^{\neq} - (V_{C_5H_5N} + V_{C_2H_5I}) - nV_0, \tag{9}$$

where $V^{\neq}$ is the molar volume of the solvated activated complex, $V_{C_2H_5N}$ and $V_{C_2H_5I}$ are the molar volumes of pyridine and ethyl iodide, and V_0 is the molar volume of the solvent. Equation (9) is differentiated with respect to V_0, considering that the value of n is independent of pressure (over the pressure range studied).

$$\left(\frac{\partial \Delta V^{\neq}}{\partial V_0}\right)_T = \frac{\partial}{\partial P}[V^{\neq} - (V_{C_5H_5N} + V_{C_2H_5I})]\left(\frac{\partial P}{\partial V_0}\right)_T - n. \tag{10}$$

Let us examine the derivative from the expression in square brackets in the right-hand part of equation (10). It can be assumed that this derivative is positive. This assumption would be quite obvious if we were comparing the contraction of the unsolvated activated complex and the starting materials. As we have already mentioned above, in addition reactions without the participation of solvent, the negative value $\Delta V^{\neq}$ decreases with an increase in pressure [7]. The participation of solvent in the activated complex makes this assumption less obvious; however, it should be considered that the solvation envelope is more dense than the solvent itself and therefore its compressibility should be very small. Since the value $(\partial P/\partial V_0)_T$ is negative, consequently we may write the following equation instead of (10):

$$\left(\frac{\partial \Delta V^{\neq}}{\partial V_0}\right)_T = -(n + \beta), \tag{11}$$

where

$$\beta = -\frac{\partial}{\partial P}[V^{\neq} - (V_{C_5H_5N} + V_{C_2H_5I})]\left(\frac{\partial P}{\partial V_0}\right)_T; \qquad \beta > 0. \tag{12}$$

Thus, by investigating the relation of $\Delta V^{\neq}$ to V_0 at different pressures and constant temperature, with the assumptions given above we may find the upper limit for n, i.e., the number of solvent molecules solvating the activated complex.

Figure 2 shows the relation between the values of $(-\Delta V^{\neq})$ we found for the reaction in alcohol over the pressure range investigated. It was found that this relation is satisfactorily represented by a straight line with a slope $n+\beta = 1.7$. Hence it follows that $n \leq 1.7$. We obtained an analogous results by processing the experimental data from [2] on the effect of pressure on the rate constant of the reaction of pyridine with ethyl iodide in acetone* (Fig. 3). In this case $n \leq 2.0$.

Consequently, the examination of the problem under consideration, on the basis of equations (9) to (11), not only qualitatively confirmed the previous conclusion on the considerably lower solvation of the activated complex in comparison with ions of the reaction product, but also made it possible to estimate that the solvation envelope of the complex contains not more than two solvent molecules.

SUMMARY

1. We measured the decrease in volume of the system accompanying the reaction of pyridine with ethyl iodide at atmospheric pressure in ethanol at 50° and in acetone at 40° and also the electrical conductivity of solutions of N-ethylpyridinium iodide under the given conditions.

2. In the reaction studied, the decrease in volume as a result of solvation of the activated complex by solvent molecules is considerably less than in the solvation of ions of the reaction product.

3. On the basis of certain assumptions formulated in the work, we approximately estimated the degree of solvation of the activated complex. This estimate made it possible to surmise that the activated complex in the reaction of pyridine with ethyl iodide is solvated by not more than two solvent molecules.

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••Original Russian pagination. See C.B. translation.

STRUCTURE OF SODIUM BOROSILICATE GLASSES IN RELATION TO THE PHENOMENON OF OPALESCENCE

COMMUNICATION 5. DIRECT PROOF OF THE CHEMICALLY HETEROGENEOUS STRUCTURE OF GLASSES

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In recent years doubts have repeatedly been raised [3-8] on the structural homogeneity of glasses of complex composition, postulated in the Zachariasen–Warren hypothesis of a disordered lattice [1, 2]. In previous communications [9, 10] and some other papers [11-14], data was published indicating the chemically heterogeneous structure of some sodium borosilicate glasses, i.e., the existence of regions of different composition and structure in them. However, most of these were of an indirect nature and the experiments they were based on could be interpreted from the point of view of the disordered lattice hypothesis. In particular, the sharpest objections were provoked by attempts to provide a basis for and detailize the chemically heterogeneous structure of sodium borosilicate glasses, based on a study of the submicroscopic structure of the porous products from their extraction [9, 10]. The most distinct of these objections was put forward by Belov [15, 16], who stated that glass of this composition " is a single system both in the liquid state and as a solid glass without any heterogeneity with dimensions of 40 A and above as was supposed to have been established in the work of Porai-Koshits...Oxygen atoms cannot be divided into those which are attached to silicon alone and those which are attached to boron alone (and also to sodium).... Approximately half of the oxygen atoms must be attached simultaneously to boron and silicon. From the fact that Porai-Koshits and others established the dimensions of 'pores' in extracted borosilicate glass it does not necessarily follow that the volume of these pores was originally occupied by a single boron component or predominantly by it as the walls were composed only of the Si component. This 'geometry' which Porai-Koshits measured in the extracted glass was not the original one" [15]. In the opinion of Belov, the formation of pores is the result of the action of the extracting agent on weak positions in the chemically homogeneous glass, arising during the transition of boron atoms from triple to quaternary coordination.

The problem of the structure of sodium borosilicate glasses was repeatedly discussed at the 2nd conference on the vitreous state and in the resolutions of the conference it was recommended that "the study of sodium borosilicate glasses be developed." From all this it follows that the detection of the chemically heterogeneous structure of glasses by any direct method is of fundamental interest.

EXPERIMENTAL

Investigation procedure. The failure of attempts to obtain low-angle scattering of x-rays from glasses was regarded by supporters of the disordered lattice theory as one of the most important facts confirming this hypothesis. However, no allowance was made for the difficulty of detecting this effect due to the extremely low intensity of low-angle scattering by objects with small heterogeneities and insignificant differences in electron densities. There have not been even rough estimations of the intensity of low-angle scattering in comparison with the intensity of the primary beam or of the exposures necessary to detect it.

In this respect, sodium borosilicate glasses are a very suitable subject for investigation; according to a study of their porous extraction products [9, 10] by appropriate thermal treatment of the glasses, it is possible to increase the dimensions of the regions of heterogeneity to 1000 A and above and thus increase the intensity of low-angle scattering. At the same time it should be remembered that coarse particles (> 500 A) scattering x-rays in the same region of low angles in which there is strong parasitic scattering by the collimating slits in a normal slit camera.

The low-angle apparatus with collimation by Kratky's method [17], which we used with some changes and improvements, is free from this drawback to a considerable extent. In order to get rid of parasitic scattering by air, which was found to be stronger than low-angle scattering by glasses, the collimating frame, sample, and receiver were placed in a single vacuum system. A plan of the apparatus, showing the most important dimensions, is given in Fig. 1.

The x-ray source was a BSVI-Si tube with a line focus; the beam was filtered with a nickel filter, 0.015 mm thick. To allow for errors due to incomplete monochromatization of the primary beam, a comparison was made of low-angle x-ray diffraction patterns of the same samples of porous glass obtained, in one case, on the new apparatus with filtered radiation and, in the other, on a normal slit camera with strictly monochromatized radiation. This comparison showed that there was complete coincidence of the intensity curves from the greatest scattering angles to an angle of 18'; only in the region of angles of 18' to 7' was the curve obtained with filtered radiation somewhat displaced toward smaller scattering angles, which must lead to a very slight increase in the calculated dimensions of the scattering regions.

The frame collimator was made of TF-3 glass and the edges of the inlet slit and the trap, from molybdenum. The trap was arranged so that it covered the upper sharp edge of the primary beam by 0.05 mm. The scattering was recorded with an Agfa Laue Film x-ray plate. Only the upper part of the plate was used for calculation and photometric measurements were made with a MF-4 recording microphotometer.

In addition to low-angle x-ray scattering we also measured the intensity of scattering of visible light through an angle of 90°. This was done with a photometer, consisting of an incandescent lamp, a UM-2 monochromator, an FÉU-19 photomultiplier, and a dc amplifier.

The investigation was carried out with a glass containing 7 mol. % of Na_2O, 23 mol. % of B_2O_3, and 60 mol. % of SiO_2. After solidifying from the melt, the starting glass (sample 1) was annealed at 500°. The other samples were prepared from the starting sample by annealing at 600 and 650° with subsequent quenching in air. Samples intended for measuring the intensity of visible light scattering were made in the form of rectangular parallelepipeds with polished faces. For the preparation of porous glasses, all the samples were powdered and treated with HCl and KOH as described previously [9].

The form of the samples of unextracted glasses was found to be very important for obtaining low-angle x-ray diffraction patterns. In attempts to use powdered samples, we observed low-angle scattering which was in no way connected with the internal structure of the object investigated; it depended on the degree of dispersion of the sample and was evidently produced by the surface structure of the individual grains. This was confirmed by the fact that such low-angle scattering was obtained for powdered samples of vitreous silica, microscope slide glass and Pyrex glass. When x-ray patterns were obtained for the same glasses in the form of thin polished plates, no traces of low-angle scattering were detected even with exposure of the order of 100 hr, while powdered samples gave intense scattering in 2-3 hr. Therefore, samples of nonporous sodium borosilicate glasses were always used in the form of polished plates 0.2-0.3 mm thick. In this case the exposure depended on the thermal treatment of the glass and varied from 15 to 100 hr. In the case of porous glasses, the exposure was of the order of a few minutes and, due to this, the scattering of the grain surface did not appear.

Experimental results. The main purpose of the work was to obtain low-angle scattering by sodium borosilicate glasses before their extraction and to compare it qualitatively and quantitatively with the scattering of porous glasses. It required 100 hr to obtain an x-ray diffraction pattern of the starting glass 1, in which the sodium borate component was in the most finely disperse state for the given series of samples. An exposure of only 15 min was required to obtain an x-ray diffraction pattern of approximately the same maximum blackening from porous glass obtained from glass 1 by treatment with hydrochloric acid. After further treatment of the porous glass with 0.5 N KOH solution for 2 hr, during which the channels were freed from finely disperse silica [9], the exposure was reduced to 7 min. As the regions of chemical heterogeneity grew during thermal treatment,

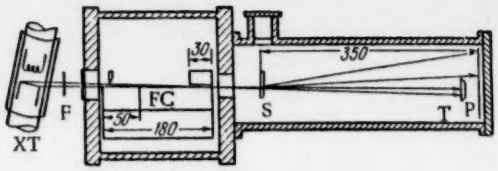

Fig. 1. Schematic diagram of low-angle apparatus with collimation by Kratky's method: XT) x-ray tube; F) filter; FC) frame collimator; S) sample; T) primary beam trap; P) x-ray plate. The dimensions are given in millimeters.

the necessary exposure times systematically decreased and for glasses where these regions were largest (heated at 650° for 8 hr), they equaled 15-20 hr; an exposure of the order of 1 min was required to obtain x-ray diffraction patterns of the corresponding porous glass.

Figures 2-4 show microphotometric curves of the three unextracted glasses mentioned (curves a), the corresponding porous glasses after treatment with HCl (curves b), and the glasses after additional treatment with KOH (curves c). In each case these curves were similar to each other, which indicates the similarity of the size of the regions occupied by the sodium borate component of the glasses and the size of the pores obtained during extraction. This similarity is expressed even more clearly on the intensity curves presented in Fig. 5, where the solid curves refer to unextracted glasses and the broken lines to porous glasses. Figure 5 also shows that the curves of the intensity of the starting and porous glasses in relation to the thermal treatment of the former are completely symbatic; with an increase in temperature or duration of heating, the curves were systematically displaced toward lower scattering angles, which indicates a simultaneous increase in both the size of the regions of heterogeneity in the starting glasses and the pores in the extracted glasses.

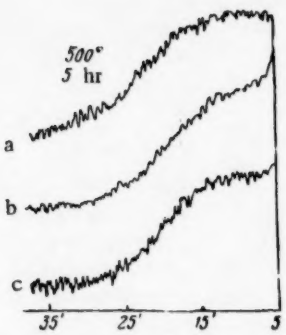

Fig. 2. Microphotometric curves of low-angle x-ray scattering for sample 1: a) unextracted starting glass; b) porous glass after HCl treatment; c) porous glass after HCl and KOH treatment.

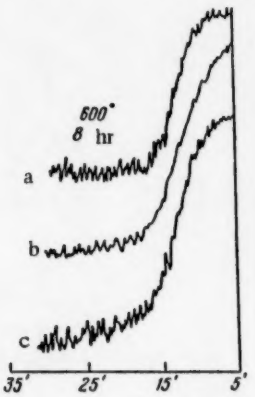

Fig. 3. Microphotometric curves of low-angle x-ray scattering for sample 5: a) unextracted glass; b) porous glass after HCl treatment; c) porous glass after HCl and KOH treatment.

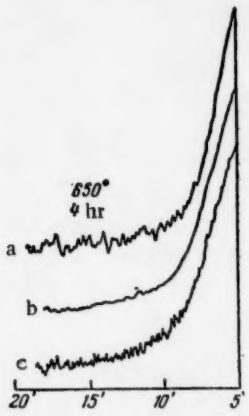

Fig. 4. Microphotometric curves of low-angle x-ray scattering for sample 9: a) unextracted glass; b) porous glass first HCl treatment; c) porous glass after HCl and KOH treatment.

As a rule, the intensity curves of the starting glasses and porous glasses that had been heated at 650° differed somewhat more appreciably than with heating at 600°. Generally speaking, there is no reason why the dimensions of the regions of heterogeneity should coincide exactly with the dimensions of the pores after extraction. To some extent this difference is explained by the different conditions for obtaining the x-ray patterns (30 kw for starting glasses and 15 kw for the porous glasses), however, the main reason is apparently the slight difference between the thermal treatment of the starting glasses and those intended for extraction; small differences in temperature at ~650° should lead to appreciable structural changes as compared with structural changes at ~600°.

Sample No.	Annealing temperature in °C	Annealing time in hr	R_{pa} in A (starting glass)	R_{po} in A (porous glass)	Light scattering intensity
1	500	5	105	110	1
2	600	1	125	—	1,4
3	600	2	—	140	1,8
4	600	4	160	165	2,2
5	600	8	175	180	3,4
6	650	1	390	310	30
7	650	2	610	450	440
8	650	3	700	540	960
9	650	4	715	560	2800
10	650	5	870	640	—
11	650	6	950	700	—
12	650	8	—	817	—

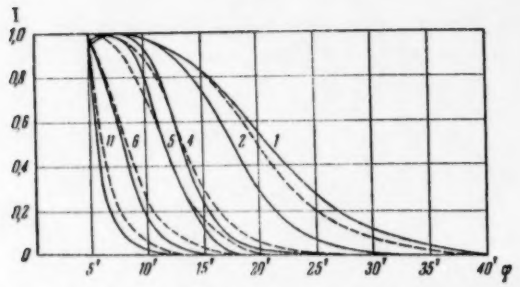

Fig. 5. Intensity curves of low-angle x-ray scattering for starting (solid lines) and porous (broken lines) glasses. Thermal treatment of glasses: 1) 500°, 5 hr; 2) 600°, 1 hr; 4) 600°, 4 hr; 5) 600°, 8 hr; 6) 650°, 1 hr 11) 650°, 6 hr.

The experimental data obtained make it possible to calculate the dimensions of the regions of heterogeneity of the starting glasses (which will subsequently be referred to as "particles" for brevity) and the dimensions of the pores in extracted glasses. Where there was a maximum on the intensity curve, which appeared more rarely after the introduction of a collimation correction for the length of the slit limiting the primary beam, the radius was calculated from the position of this maximum. When there was no maximum, the radius was calculated by the method of tangents [9] with the introduction of a collimation correction for the slit width.

The results of calculations of the radii of particles (R_{pa}) and pores (R_{po}) and data on the thermal treatment of the starting glass are given in the table; it also gives the relative values of the intensity of visible light (λ 337 mμ), measured at an angle of 90° to the incident beam. As units for the measurement we chose the intensity of light scattering in sample 1. After thermal treatment, samples 2-5 remained transparent, similar to sample 1. Glasses annealed at 650° had a different degree of opalescence, which was readily detected visually. For samples 10-12, the intensity of visible light scattering had increased so much that it was impossible to measure it on our apparatus.

As has already been stated, samples of unextracted glasses were made in the form of polished plates, 0.2-0.3 mm thick. However, the surface of the glasses could have been partly extracted during the polishing process. In order to make certain that the low-angle scattering of x-rays was caused by the existence of heterogeneities in the whole volume of the glass and not the surface structure of the polished plates, we carried out additional experiments with plates of different thickness and calculated the possible change in the intensity of low-angle scattering both for volume and surface scattering. These experiments unequivocally confirmed the fact that the low-angle scattering we observed was caused by the internal, chemically heterogeneous structure of sodium borosilicate glasses and that the role of surface scattering was negligible in the given case.

The similarity of the intensity curves of the starting and porous glasses implies similarity in the size, form, and relative disposition of the particles and pores. This circumstance makes it possible to calculate, from the ratio t/t' of the exposures of the starting and porous glasses, the difference between the electron densities of the silica glass and the second component of the glass, which may also contain silica in addition to sodium oxide and boric anhydride; here it is necessary to allow for the difference in the absorption coefficients τ and sample thickness $\underline{d}$ of the starting and extracted glasses. Allowance for these factors leads to the following expression for the difference in electron densities:

$$|\Delta\rho| = \rho_{SiO_2}\sqrt{\frac{S}{S'}\frac{t'}{t}\frac{d'}{d}e^{\varkappa d-\varkappa' d'}}, \quad (1)$$

where ρ_{SiO_2} is the electron density of vitreous silica, equal to 0.663 e/A^3 and S/S' is the ratio of the blackenings at a definite scattering angle for the starting and porous glasses; the symbols without dashes refer to starting glasses and those with dashes, to extracted glasses.

For glasses annealed at 600°, the difference in electron densities according to formula (1) is found to equal:

$$|\Delta\rho| = 0{,}03 \pm 0{,}01 e/A^3.$$

As this method may be used for determining only the absolute value of the difference $|\Delta\rho|$, then the electron density of the second component of the glass in this case equals either 0.633 e/A^3 if it is less than the electron density of the silica skeleton, or 0.693 e/A^3 in the opposite case. As the density of sodium borosilicate glasses is higher than the density of vitreous silica, the second value is preferable to the former. We should note that neither of these values coincide with the electron density of sodium triborate and therefore the latter cannot be considered as the second component of the glass.

As Fig. 5 shows, the intensity curves of glasses annealed at 650° do not coincide with the intensity curves of the corresponding porous glasses in any section; this indicates the different value of the form factors (evidently produced by the different heating temperature of the samples) and makes it impossible to make an analogous calculation from formula (1) for these glasses.

After treatment of the starting glasses with hydrochloric acid, the main channels of the silica skeleton are found to be more or less filled with highly disperse silica (which we previously named "secondary silicic acid" [9] and Dobychkin called "a fine silica lattice" [18]). This highly disperse silica may be dissolved and removed by additional treatment of the porous glass with a weak alkali solution [9]; the intensity curves of low-angle scattering after this treatment hardly change their form (Figs. 2-4). The use of formula (1) in this case is quite legitimate (the form factors coincide) and it is possible to calculate the difference between the electron densities of the silica skeleton and the highly disperse silica. For glasses annealed at 600°, regardless of the annealing time, it was found to equal 0.52 e/A^3 and for glasses annealed at 650°, 0.27 e/A^3; in other words, the electron density of the highly disperse silica itself with firing at 600° was ~0.14 e/A^3, while with an increase in temperature to 650°, it increased to 0.39 e/A^3, i.e., by a factor of almost three. Therefore, it is extremely probable that, with an increase in temperature, there is a change in the composition of the second component of the glass, namely, an increase in its silica content. On the other hand, the independence of the difference ($\Delta\rho$) and electron density of the highly disperse silica of the time that the glass was heated at the given temperature indicates the constancy of the composition of the second component of the glass, despite the continuous increase in the size of the regions of heterogeneity as a result of this heating. These results are in good agreement with the sorption investigations of Zhdanov [19], who showed that the duration of heating of starting glasses at a definite temperature had no effect on the internal surface, volume, and size of the pores of glasses extracted with hydrochloric acid.

DISCUSSION OF EXPERIMENTAL RESULTS

The observation of low-angle diffraction of x-rays for any glass is a direct demonstration of its submicroscopic heterogeneous structure. Therefore, a communication on this fundamentally important fact requires careful checking. There have already been reports on the observation of low-angle scattering of x-rays by certain glasses, but this was subsequently disproved [20, 21]. Apart from the reasons for false effect pointed out by Cartz [21], we should also note that Hoffman and Statton [20] used powdered samples, which, according to our investigation, produce quite intense scattering by the grain surface.

More careful attention should be paid to the work of Brumberger and Debye [22], who, according to their statement, obtained low-angle scattering of x-rays by "some porous and nonporous glasses" and observed a relation between this scattering and the thermal treatment of glasses of the Vycor and Pyrex types. However, a further examination of the article forces us to the conclusion that low-angle scattering was obtained by the authors

only for porous glasses prepared either from sodium borosilicate glasses by extraction or from highly disperse vitreous Pyrex by sintering; in the first case,the investigation and its results are very close to those we published in previous communications [9, 10] and,in the second case, like Hoffman and Statton [20], the authors used powdered disks of sintered Pyrex glass (ultrafilters), i.e., these should also give false low-angle effects, distorting the results of their work, which therefore requires checking.

Our calculations explain the failure of previous attempts to detect low-angle scattering by glasses. The main reasons are the extremely low differences between the electron densities of the regions of heterogeneity and the very small size of the latter. In the sodium borosilicate glasses we investigated, the dimensions of the regions of heterogeneity were large enough for detection of the low-angle effect by means of a luminosity apparatus. This result, the conclusiveness of which is emphasized by the great similarity of the diffraction patterns of the starting and porous glasses, is not compatible with the disordered lattice hypothesis of Zachariasen and Warren and is a direct demonstration of the chemically heterogeneous structure of the glasses we investigated, contrary to the opinion of Belov which was presented at the beginning of the article.

Apart from establishing this fundamental fact, our investigation gave new facts, confirming and developing previously presented opinions of the authors on processes occurring in sodium borosilicate glasses during their thermal treatment [9]. It is increasingly obvious that the increase in the dimensions of the regions occupied by the second component of the glasses is the result of the superposition of two processes: growth at the expense of the silica skeleton surrounding them (i.e., with a change in their composition) and merging of separate regions to give coarser ones without a change in their composition (overcondensation process [18]). In actual fact, the sharp increase in the electron density of the highly disperse silica remaining in the coarse channels after extraction with an increase in the firing temperature of the starting glass (from 0.14 e / A^3 at 600° to 0.39 e/ A^3 at 650°) indicates growth of the regions at the expense of the surrounding silica. Enrichment in silica involves an increase in the viscosity of the second component and this process ceases if the temperature stops rising. On the other hand, the independence of the electron density of the highly disperse silica of the heating time of the original glass at a given temperature (in the opalescence zone) indicates that in this case the increase in the size of the regions proceeds by overcondensation; however, the mechansim of overcondensation requires further elucidation. It is extremely probable that further investigations in this direction will shed light on the anomalous changes with temperature of the density, refractive index, and other properties of sodium borosilicate glasses which are capable of extraction [23].

Let us examine another problem that was discussed in a previous communication [9]. Abe [11] explained the opalescence of sodium borosilicate glasses by their deposition of microscopic crystallites of cristobalite. It was previously pointed out that there is a logical inconsistency in this statement, but since the author quoted an experimental fact, namely, that x-ray diffraction patterns with cristobalite lines were obtained, we obtained normal x-ray patterns of the glass. We obtained the patterns in a vacuum camera, 57.3 mm in diameter, using CuK_α radiation monochromatized by reflection from a urea nitrate monocrystal. The same plates on which low-angle scattering was detected were used as samples. As a result we obtained diffraction patterns which were typical of vitreous substances without traces of discrete lines, regardless of the degree of opalescence of the glass.

Are the glasses investigated an exception? Have other complex glasses or even sodium borosilicate glasses of other composition a chemically heterogeneous structure? A direct demonstration of the heterogeneous structure of other glasses would be the detection of low-angle scattering by them, but up to now this has only been detected for sodium borosilicate glasses which are capable of extraction. Data indicating the submicroheterogeneous structure of many complex glasses were presented by us previously [9]. We should point out yet another circumstance. Previous investigations of a number of properties of sodium borosilicate glasses which are capable of extraction and the structure of their extraction products [9, 10, 24] indicate definitely that the dimensions of the regions of heterogeneity in the starting glasses may be changed continuously by appropriate thermal treatment from a few tens of angstroms (according to adsorption data, from R = 20 A [9]) to 1000 A and above. Moreover, in the present work, low-angle scattering was detected only for glasses of this series in which the radius of the regions of heterogeneity exceeded 100 A. A simple calculation shows that for the detection of low-angle scattering by glasses with regions 50 A in size, even with our light sensitive apparatus, it would be necessary to have an exposure of the order of 2000 hr (the corresponding porous glass with a pore radius of 50 A required a two-hour exposures, while glasses with larger pore radii required a few minutes). Thus, even in this obvious case, it is necessary to overcome purely technical difficulties of creating a more light-sensitive apparatus with

even better collimation (to prevent the appearance of the weakest parasitic effects, which appeared on our apparatus with exposures of more than 100 hr). Such an apparatus should help to solve conclusively the problem of the chemically heterogeneous structure of other complex glasses and, in the first instance, those for which this structure has been detected only by insufficiently direct methods (see, for example, [7, 9, 25]).

SUMMARY

1. Low angle scattering of x-rays was obtained for the first time for a number of samples of sodium borosilicate glasses, demonstrating their chemically heterogeneous structure. We determined the dimensions of the regions of heterogeneity of the glasses investigated and these depended on the thermal treatment of the glasses and were close to the dimensions of the pores of the corresponding extracted glasses.

2. The increase in the regions of heterogeneity with a rise in temperature occurred at the expense of the silica surrounding them, i.e., with a change in composition, and also by overcondensation without a change in composition of the merging regions.

3. By comparing the intensities of the low-angle scattering of the starting and extracted glasses we determined the difference in the electron densities of the silica skeleton and the second component of the glass, which was found to equal approximately 0.03 e/A^3. We estimated the intensity of low-angle scattering in the case of glasses with small regions of heterogeneity and found the reasons for the failure of attempts to detect low-angle scattering of x-rays by glasses of other compositions.

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CHAIN-THERMAL FLAME PROPAGATION

COMMUNICATION 4. EFFECT OF CHAIN BRANCHING AND TERMINATION

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We previously obtained the relations for determining the rate of flame propagation [1, 2] without taking into account branching and the rate of chain termination. The effect of the rate of second order chain termination was only estimated in the first article [1].

Derivation of relations. As before, the chain mechanism of decomposition, including two active centers which react in sequence with the starting material and regenerate each other, is represented as a simplified scheme with an active center of one type [1]:

$$A \rightarrow 2P \quad \text{initiation} \qquad Q_R = h_R R(T');$$

$$P + A \rightarrow 2C + P, \quad Qn = hFn = hK(T')n_A n;$$

$$P + A \rightarrow C + 2P \quad \text{branching} \qquad Q_v n = h_v Vn = h_v K_v(T')n_A n;$$

$$\left(P \rightarrow \text{linear termination}\right.$$

$$P + P \rightarrow A \quad \text{termination} \qquad Q_w n^2 = h_w W(T')n^2.$$

The expressions for the heat evolution rates are written on the right hand side. Here h_i is the heat effect, K_i is the reaction rate constant, W is the second order chain termination rate constant, n_A is the concentration of the material A, and n is the concentration of the active center P.

The rate of the linear chain branching may also be written as $K_v n_A n = iKn_A n$, from which $i = V/F = K_v/K$, where i is the chain branching coefficient. When there is linear chain termination, $i < 0$ and the relation remains true for i.

When the diffusion coefficient of the starting material A equals the thermal conductivity coefficient ($\lambda = c\rho D_A$), we obtain the following system of equations for the stationary distribution of a laminar, one-dimensional flame.

$$\lambda p \frac{dp}{dT'} - Bcp + Q_\Sigma n + Q_w(n^2 - n_i^2) - Q_R = 0, \tag{1}$$

$$D\frac{d^2n}{dx^2} - B\frac{dn}{dx} + R + Vn - W(n^2 - n_i^2) = 0, \tag{2}$$

where $B = u\rho$; $D = \rho D_p$; $Q_\Sigma = Q + Qv$; $p = \frac{dT'}{dx}$; x is the coordinate normal to the plane of the flame, u is the flow rate

along axis $\underline{x}$, T' is the temperature in °K, ρ is the density, n_λ is the dimensionless, weight concentration of the starting material, $\underline{n}$ is the dimensionless weight concentration of the active center, D_A is the diffusion coefficient of the starting material, D_p is the diffusion coefficient of the active center, λ is the thermal conductivity of the mixture, $\underline{c}$ is the heat capacity at constant pressure, and n_t is the flowing equilibrium concentration of the active center.

The index "0" will denote values in the initial state ($T' = T'_0$) and index "Γ", in the final state ($T' = T_\Gamma$). The extreme values of the functions of the chemical reaction rates: $R(O) = R(T_\Gamma) = 0$, $Q(O) = Q(T_\Gamma) = 0$, $Q_v(O) = Q_v(T_\Gamma) = 0$, $[Q_\omega(n^2 - n_t^2)]_0 = [Q_\omega (n^2 - n_t^2)]_\Gamma = 0$, thus, $n_0 = n_{t0}$ as $n_\Gamma = n_{t\Gamma}$, where we assume that $T = T' - T'_0$. The limiting conditions for (1) and (2) coincide with those assumed in [1].

The active center concentration n_m at temperature $T = T_m$, which corresponds to the maximum value of the temperature gradient $p = p_m$, we will write [1] in the following form:

$$n_m = t + [R_m + V_m n_m - W_m (n_m^2 - n_t^2) - Blp_m] N,$$

$$\text{where } l = \frac{n_\Gamma - n_0}{T_\Gamma},\ T_\Gamma = T'_\Gamma - T'_0,\ t = n_0 + lT_m,\ r = T_m(T_\Gamma - T_m), \tag{3}$$

$$T_m = T'_m - T'_0,\ N = \frac{r}{2D_m p_m^2}.$$

From (3) we have:

$$W_m N n_m^2 + (1 - V_m N) n_m - (t - Blp_m N + R_m N + W_m N n_t^2) = 0. \tag{3'}$$

By solving quadratic equation (3') we find $n_m = n(T_m; p_m)$:

$$n_m = \frac{-(1 - V_m N) \pm \sqrt{(1 - V_m N)^2 + 4W_m N (t - Blp_m N + R_m N + W_m N n_t^2)}}{2W_m N}. \tag{4}$$

From (1) when $p = p_m$ and $(dp/dT)_m = 0$ [1] we have:

$$-Bcp_m + Q_{\Sigma m} n_m + Q_{wm} n_m^2 - Q_{pm} = 0, \tag{5}$$

where $Q_p = Q_w n_t^2 + Q_R$.

Substituting n_m from (4) in (5), when $B = \eta p_*$ [1, 2]:

$$p_*^6 \eta A_1 - p_*^4 (\eta^2 A_2 + \eta A_3 + A_5) - \\ - p_*^2 (\eta A_4 - A_6 - \eta A_7 + A_8) + A_9 = 0, \tag{6}$$

where $A_1 = 4cD_m^2 f$,

$$A_2 = (c + lh_w)^2 gr^2,$$

$$A_3 = 2D_m r (c + 2cV_m f - lh_w - 2tlQ_{wm} f - 2ctfW_m),$$

$$A_4 = r^2 (lQ_{\Sigma m} - cV_m + lV_m h_w - cV_m^2 f),$$

$$A_5 = 4D_m^2 (t^2 f Q_{wm} + th_w - fQ_{pm}),$$

$$A_6 = 2D_m tr (Q_{\Sigma m} + V_m h_w),$$

$$A_7 = 2r^2 (lfQ_{wm} R_{pm} + cfW_m R_{pm} - cgQ_{pm} - lfW_m Q_{pm}),$$

$$A_8 = 2D_m r (2tR_{pm} Q_{wm} f + Q_{pm} - 2tfW_m Q_{pm} + 2fV_m Q_{pm} + h_w R_{pm}),$$

$$A_9 = r^3(Q_{\Sigma m}R_{pm} + V_m h_w R_{pm} + fV_m^2 Q_{pm} + 2fW_m R_{pm}Q_{pm} + + V_m Q_{pm} - fQ_{wm}R_{pm}^2 - gQ_{pm}^2),$$

$$f = \frac{h_w}{Q_{\Sigma m}},\quad g = \frac{W_m}{Q_{\Sigma m}} \text{ and } R_{pm} = R_m + W_m n_t^2.$$

By determining p_*^2 from the cubic equation (6), we find the flame propagation rate

$$u_0 = \frac{B}{\rho_0} = \frac{1}{\rho_0}\eta p_*,$$

$$\text{where [1,2] } \eta = \frac{4D_0}{\varkappa T_m},\quad \varkappa = \frac{cD_0}{\lambda_0},\ D_0 = D_m q, \tag{7}$$

$$q = \frac{\mu_0}{\mu_m}\left(\frac{T_0'}{T_m'}\right)^{a-1} \text{ when } D_P \sim (T')^a.$$

If, as was done before [1, 2] we neglect the value of the active center initiation rate, i.e., if we assume $A_7 = A_8 = A_9 = 0$ (we also assume that $W_m n_t^2 \approx 0$), then from (6) we obtain a biquadratic equation for determining p_*.

$$p_*^4 \eta A_1 - p_*^2(\eta^2 A_2 + \eta A_3 + A_5) - (\eta A_4 - A_6) = 0, \tag{8}$$

hence

$$p_*^2 = \frac{(\eta^2 A_2 + \eta A_3 + A_5) - \sqrt{(\eta^2 A_2 + \eta A_3 + A_5)^2 + 4\eta A_1(\eta A_4 - A_6)}}{2\eta A_1}. \tag{9}$$

Resolving the radical in formula (9) into a series, we find the approximate relation

$$p_*^2 \approx \frac{A_6 - \eta A_4}{\eta^2 A_2 + \eta A_3 + A_5}. \tag{10}$$

Now from (7) and considering (10), we obtain

$$u_0 = \frac{1}{\rho_0}\,\eta\sqrt{\frac{A_6 - \eta A_4}{\eta^2 A_2 + \eta A_3 + A_5}}. \tag{11}$$

Let us make another approximation, assuming that $A_4 \approx A'_4 = r^2(lQ_{\Sigma m} - cV_m)$, $A_3 \approx A'_3 = 2D_m r(c + 2cV_m f)$ and $A_5 \approx A'_5 = 0$. Then, according to (7) and (11) and taking into account the definitions accepted above, we have:

$$u_0 = \varphi\psi\frac{1}{\rho_0}\sqrt{\frac{n_\Gamma Q_{\Sigma m} D_m}{2cT_\Gamma}} = \varphi\psi\frac{1}{2\rho_0}\sqrt{n_\Gamma\left(K_m + \frac{h_v}{h}K_{vm}\right)(\rho D_P)_m}, \tag{12}$$

where

$$\varphi = 2\sqrt{\frac{2q}{\varkappa}\left(1 - \frac{2q}{\varkappa}\right)}, \tag{13}$$

$$\psi = \sqrt{\frac{1 + \frac{K_{vm}}{K_m}\left[\frac{h_v}{h} + \frac{\varkappa}{(\varkappa - 2q)}\frac{h_w}{h} + \frac{2qn_{Am}}{t(\varkappa - 2q)}\right]}{1 + \frac{K_{vm}}{K_m}\left[\frac{h_v}{h} + 2\frac{h_w}{h}\right] + \frac{2q}{\varkappa}\frac{W_m}{K_m}}} \qquad (14)$$

or more approximately

$$\psi = \sqrt{\frac{1 + i\,\frac{2qn_{Am}}{t(\varkappa - 2q)}}{1 + \frac{2q}{\varkappa}\frac{W_m}{K_m}}}. \qquad (15)$$

If we assume in relations (12) and (14) that $k_{vm} = 0$ and $w_m = 0$, then $\psi = 1$ and from (12) we have an equation for determining the flame propagation rate which was obtained previously [1, 2] without taking into consideration chain branching and termination. As previously [2], the coefficient φ expresses the relation of u_0 to the ratio of the active center diffusion coefficient multiplied by the heat capacity and density to the thermal conductivity (value χ). However, in the more complex case being examined here, the value χ also enters the relation for ψ (14).

Let us examine the effect of second order chain termination ($W_m \neq 0$), linear chain branching ($K_{vm} > 0$), and linear chain termination ($K_{vm} < 0$) according to the approximate, but simpler, relation for ψ (14). The effect of second order termination rate depends on the ratio of constant W_m to constant K_m. Therefore, apparently, the effect of second order chain termination will have a greater effect the lower the combustion temperature T_Γ', with all other conditions the same, as with a fall in T_Γ', K_m decreases and W_m increases. A decrease in χ will increase the extent of the effect of W on u_0. When there is linear chain branching the effect of W will be felt less, the greater the branching rate constant K_{vm}. The effect of linear chain branching on u_0 will be greater, the smaller $t = n_\Gamma/2$ (with a fall in n_Γ there will be a relative increase in the role of the chain initiation and branching rate, as the active center diffusion flow decreases) and the smaller χ, as then the number of active centers brought into the reaction zone by diffusion will be relatively lower.

The effect of linear chain termination ($K_v < 0$ or $i < 0$) will be greater, the smaller n_Γ, with all other conditions the same (the relative role of chain branching increases with a fall in n_Γ). This effect is felt mainly as a result of the change in the second term in the numerator (14) or (15). A decrease in χ increases the extent of the effect of the linear chain termination rate on u_0. K_v is also included in relation (12) and reduces u_0 if $h_v \neq 0$.

Numerical calculations. Using the relations obtained above we made numerical calculations for a hydrazine decomposition flame which was previously investigated in [1]. All the starting data required for calculating the flame propagation rates were taken without alteration from [1]. Let us repeat the expression for the rate constants.

$$K_m = Z_A \frac{1}{\mu_P}\rho_m^2 \exp(-E/RT_m'); \quad R_m = Z_P \frac{n_{A_m}}{\mu_A}\mu_P\rho_m \exp(-E_P/RT_m'),$$

$$W_m = Z_0 \frac{1}{\mu_P\mu_M}\rho_m^3.$$

Additional initial data used in the present calculations are as follows: $h_v = 0$, $Q_v = 0$, $Q_\Sigma = Q$, $h_w = 3 \cdot 10^3$ cal/g, $h_R = 2 \cdot 10^3$ cal/g.

The coefficients of equation (6) were calculated and it was established that p_* calculated from (6) was practically the same as p_* calculated from (8). This justifies the assumption, made previously [1] and accepted in the derivation of equation (8), that the initiation rate of active centers may be neglected as a considerable

TABLE 1

The Effect of Chain Branching and Termination on the Flame Propagation Rate u_0 (cm/sec) for a Hydrazine Decomposition Flame at $T_0' = 300$ °K and $T_\Gamma' = 1950$ °K [1]

Linear branching $\underline{i}$	0	0	$5 \cdot 10^{-3}$	10^{-2}	$5 \cdot 10^{-2}$	10^{-1}
Second order chain termination	$W = 0$	$W \neq 0$				
By rel. (7) and (9)	146	140	144	148	173	202
By rel. (12), (13), and (14)	146	135	139	142	164	181
By rel. (12), (13), and (15)	146	137	143	148	186	224

TABLE 2

The Effect of Chain Branching and Termination on the Flame Propagation Rate u_0 (cm/sec) of Hydrazine Decomposition at $T_0' = 300$ °K and $T_\Gamma' = 1280$ °K

Linear branching	0	0	$5 \cdot 10^{-5}$	10^{-4}	$5 \cdot 10^{-4}$	10^{-3}	$5 \cdot 10^{-3}$
Second order termination	$W = 0$	$W \neq 0$					
By (7) and (9)	7,35	5,10	5,45	5,79	8,05	10,2	20,3
By (12), (13), and (14)	7,35	5,11	5,47	5,82	8,08	10,2	20,3
By (12), (13) and (15)	7,35	5,11	5,57	5,82	8,08	10,2	20,4

* The flame propagation rate when $\varphi = 1$ was given in [4].

number of them are transferred by diffusion. Table 1 gives the value of u_0 for a hydrazine decomposition flame at a combustion temperature $T_\Gamma' = 1950$° K [1]. It follows from a comparison of the data in the second column ($i = 0$, $W = 0$) with data in the third column ($i = 0$, $W = 0$) that the second order chain termination rate has a very small effect on u_0. If $\underline{i}$ is small, calculation according to the most approximate relations (12) and (13) and using (14) and (15) gives results which are close to those obtained with relations (7) and (9). When $i = 0.1$, the error due to using relations (12) and (13), which are approximate in comparison with (7) and (9), and (14) or (15) is approximately 10%.

The value $i > 0$, which is needed for compensating for the effect of the second order chain termination rate, was estimated in [1]. The data in Table 1 confirm the accuracy of this estimation.

Table 2 gives u_0 for a hydrazine decomposition flame with a combustion temperature $T_\Gamma' = 1280$°K. In this case second order chain termination results in a greater fall in u_0 (as compared to that calculated for $W = 0$), as the flame with a lower T_Γ' has a wider reaction zone. At a low value of T_Γ', the approximate relations (12) and (13 with (14) or (15) give results which are closer to those obtained by relations (7) and (9).

Effect of considering chain branching and termination on the pressure dependence of the flame propagation rate. The effect of pressure on u_0 was examined in [3], where relation (12) was considered when $\varphi = 1$ and $\psi = 1$. The effect of the coefficient φ will appear only as a change in combustion temperature, if one neglects the weak pressure dependence of (ρD_p) and λ. Therefore, in mixtures with low combustion temperature T_Γ', the coefficient φ will remain practically constant. In mixtures with a high value of T_Γ', the value $\underline{q}$ will increase with a fall in pressure and this will result in a change in φ, depending on the magnetude of χ. When $\chi \geq 1$, a fall in pressure p_Σ at a high value of T_Γ' will result in an increase in φ [3] and, consequently, a decrease in index $\underline{k}$, in a relation of the type $u_0 \sim p_\delta^k$.

Effect of the coefficient ψ. With a fall in P_Σ the second term in the denominator of relation (15) will decrease as $W \sim \rho^3$ and $K \sim \rho^2$. This will lead to a decrease in the index $\underline{k}$ (increase in the effect of P_Σ on u_0). A fall in P_Σ will therefore have the greatest effect in mixtures with a low value of T_Γ', since, as was shown above (see Tables 1 and 2), the second order chain termination rate then has a greater effect on u_0. With a fall in P_Σ, $t = n_\Gamma / 2$ increases. Due to this, the effect of linear chain termination will decrease (if $Kv < 0$ or $i < 0$), and this will lead to an increase in ψ (decrease in index $\underline{k}$). This effect of a fall in P_Σ will be more sharply expressed in mixtures with a low value of T_Γ' due to the faster increase in $\underline{t}$. For the same reason a fall in P_Σ will

lead to a decrease in the effect of linear chain branching (if $K_V > 0$ or $i > 0$) and, consequently, to a decrease in ψ (increase in index k). In this case too a fall in P_Σ will have the greatest effect on mixtures with low combustion temperatures.

Effect of chain branching and termination on the relation of the flame propagation rate to the diffusion coefficient and heat conductivity. The relation of u_0 to D_p and λ was examined in [2] where the change in ψ was neglected. With a decrease in $\chi = c\rho D_p/2$ the second order chain termination rate will have a greater effect on u_0 [the value ψ (15) will decrease]. Linear chain termination will have an effect in the same direction (if $K_V < 0$ or $i < 0$). A decrease in χ will lead to an increase in the effect of linear branching (15), i.e., an increase in ψ. This has already been shown qualitatively in [2] where linear branching was expressed arbitrarily as chain initiation.

SUMMARY

1. Relations were obtained for determining the rate of flame propagation taking into account the following effects: linear chain branching and termination rates, second order chain termination rates, chain initiation rates, thermal conductivity and the diffusion coefficient of the active center.

2. From these relations it follows that second order chain termination has a greater effect on the flame propagation rate, the lower the combustion temperature and the smaller the ratio of the product of the heat capacity and density and the diffusion coefficient to the thermal conductivity. With a decrease in this ratio or with a fall in the active center concentration at the combustion temperature, the effect of linear chain branching and termination on the flame propagation rate increases as in these cases there is a relative fall in the number of active centers transferred by diffusion.

3. The relations obtained were applied to two cases of hydrazine decomposition flames and the calculations illustrate the effect of second order chain termination and linear chain branching on the flame propagation rate.

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SYNTHESIS AND EXAMINATION OF THE COMPLEX-FORMING PROPERTIES OF SOME ORGANOPHOSPHORUS COMPOUNDS*

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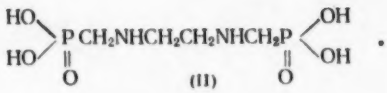
In a previous communication [1] we gave some data obtained in the examination of the complex-forming properties of (ethylenebisiminoalkylene) diphosphonic and some other aminoalkylphosphonic acids. The results showed that (ethylenebisiminoalkylene) diphosphonic acids form stable complex compounds with ytterbium and yttrium. It was of interest to continue work on the synthesis of aminoalkylphosphonic acids with the object of preparing new complex-formers, and also to compare the properties of these organophosphorus acids with the analogous amino carboxylic acids.

(Ethylenebisiminoalkylene) diphosphonic acids were synthesized by us earlier by the reaction of aldehydes or ketones with dialkyl phosphites and ethylenediamine. However, we did not then obtain the first member of this series: (ethylenebisiminomethylene) diphosphonic acid. We have now found that paraformaldehyde, like the aldehydes and ketones tried earlier, will react with ethylenediamine and diethyl phosphite, but the reaction proceeds much less readily:

$$NH_2CH_2CH_2NH_2 + 2CH_2O + 2HPO(OC_2H_5)_2 \rightarrow \underset{(I)}{[(C_2H_5O)_2OPCH_2NHCH_2]_2} + 2H_2O.$$

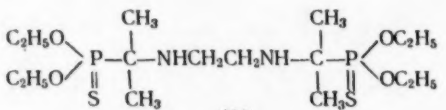
The resulting tetraethyl (ethylenebisiminomethylene) diphosphonate (I) was characterized as its picrate; the yield of the ester was about 10%. Hydrolysis of the ester with hydrochloric acid gave free (ethylenebisiminomethylene) diphosphonic acid (II):



(II)

This reaction can be carried out not only with dialkyl phosphites, but also with O-diethyl phosphorothioite or diethyl phenylphosphonite.

O-Tetraethyl (ethylenebisiminoisopropylidene) diphosphonothioate (III)

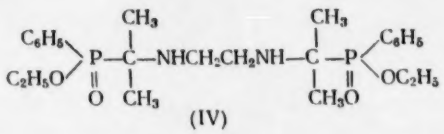


(III)

* Communication 2.

was obtained as the picrate in 26% yield. Attempts to obtain the corresponding acid were unsuccessful: on hydrolysis of the ester, sulfur was liberated.

In the reaction of ethylenediamine and acetone with diethyl phenylphosphonite we obtained diethyl(ethylenebisiminoisopropylidene)-bisphenylphosphinate (IV)

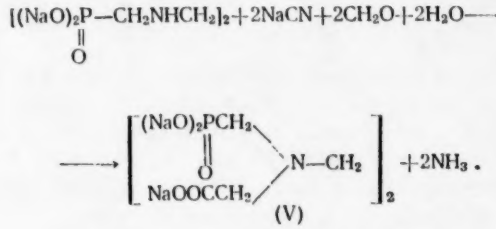


(IV)

which was also isolated as the picrate; here also decomposition of the acid occurred when the ester was hydrolyzed.

It was of interest to determine the effect of the introduction of carboxylgroups into the molecule of an (ethylenebisiminoalkylene) diphosphonic acid on its complex-forming properties. Starting with aminoalkylphosphonic and (ethylenebisiminoalkylene) diphosphonic acids, we tried to synthesize the corresponding [(carboxymethyl) amino]alkylphosphonic and { ethylenebis [carboxymethylimino) methylene]} diphosphonic acids. Comparison of different methods of preparing these substances showed that the most convenient was carboxymethylation with formaldehyde and sodium cyanide in an alkaline medium. This variant of the long-known Strecker's reaction [2] was studied in detail comparatively recently by Bersworth [3], and it was found to be suitable in our case.

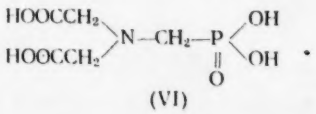
In the carboxymethylation of (ethylenebisiminomethylene) diphosphonic acid, the best results were obtained at 20-32° for a reaction time of 35-40 hours.



(V)

The acid (V) was isolated via the lead salt, which was then decomposed with hydrogen sulfide. An attempt to carboxymethylate (ethylenebisiminoisopropylidene) diphosphonic acid by this method was unsuccessful. It is probable that some steric hindrance was operative in this case.

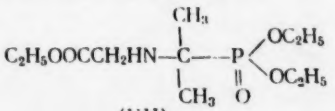
As well as {ethylenebis [(carboxymethylimino) methylene]} diphosphonic acid (V), we synthesized some (biscarboxymethylamino) alkylphosphonic acids. Although the first three members of this group were described by Swarzenbach [4], it was interesting to compare their complex-forming properties with those of other aminoalkylphosphonic acids. In the synthesis of (biscarboxymethylamino) methylphosphonic acid (VI) we applied the above-mentioned carboxymethylation reaction to aminomethylphosphonic acid



(VI)

The yield of acid was about 60%.

By the reaction of diethyl 1-amino-1-methylethylphosphonate with ethyl chloroacetate we obtained triethyl 1- (carboxymethylamino)-1-methylethylphosphonate (VII).

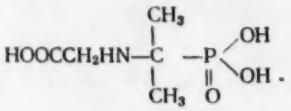


(VII)

in about 60% yield. The reaction was carried out by leaving the mixture of reactants at room temperature for many days. Rise in temperature led to a sharp reduction in yield. The same ester was prepared also by the general method for the synthesis of aminoalkylphosphonic esters [5] with glycine ethyl ester as the amine component:

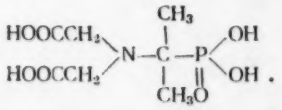
$$HPO(OC_2H_5)_2 + NH_2CH_2COOC_2H_5 + CH_3COCH_3 \longrightarrow$$
$$\longrightarrow H_5C_2OOCCH_2NHC(CH_3)_2PO(OC_2H_5)_2 + H_2O .$$

In this case the yield of ester was 25%. Under the action of hydrochloric acid the ester (VII) was hydrolyzed with formation of 1-(carboxymethylamino)-1-methylethylphosphonic acid (VIII):



(VIII)

1-Biscarboxymethylamino-1-methylethylphosphonic acid (IX) was prepared by the method used by Swarzenbach in the synthesis of 2-biscarboxymethylaminoethylphosphonic acid.



(IX)

The complex-forming powers of the compounds synthesized were tested by the previously described chromatographic method [6]. Both the amino phosphonic and also the corresponding amino polycarboxylic acids were tested chromatographically in order to obtain a comparative characterization of their complex-forming powers. The yttrium isotope Y^{91} was used in experiments with a column of KU-2 cationite. In the testing of amino phosphonic acids and the corresponding amino carboxylic acids, solutions of identical concentration, pH (6.7), and ionic strength were used. The results are presented in the table.

The activity of a complex-former was characterized by the value of V_{max}, the total volume of filtrate leaving the cationite column containing the sorbed ions of the element from the start of the washing to the attainment of a maximum concentration of the element in the eluate. Other things being equal, the value of V_{max} depends on the stability of the complex compound; and the lower it is, the higher the stability.

From a comparison of values of concentration and of V_{max} (see Table) it follows that the complex-forming powers of the compounds tested increase from the first to the third compound and from the fourth to the fifth.

Comparison of values of V_{max} for members of horizontal lines shows that, as complex-formers, all the amino phosphonic acids are stronger than the corresponding amino carboxylic acids. The difference in values of V_{max} is least for the last compound.

EXPERIMENTAL

Picrate of Tetraethyl (Ethylenebisiminomethylene) diphosphonate (I). Gradual addition was made of 1.5 g (0.05 mole) of paraformaldehyde to a stirred mixture of 6.9 g (0.05 mole) of diethyl phosphite and 1.5 g (0.025 mole) of ethylenediamine. Reaction occurred with dissolution of the paraform and rise of temperature to 70°. The reaction mixture was then heated for one hour at 85°. The resulting sirup was extracted with ten times its volume of dry ether. The ether extract was dried with sodium sulfate, and an ether solution of picric acid was then added. We obtained 1.9 g (10%) of (I); decomp. temp. 191-192° (from ethanol). Found: C 34.6; 34.5; H 4.4; 4.3; P 7.4; 7.6; N 13.6; 13.6%. $C_{24}H_{36}P_2N_8O_{20}$. Calculated: C 35.2; H 4.4; P 7.6; N 13.7%.

V_{max} (ml) on the Curves for the Elution of Y^{3+} from a Column of KU-2 Cationite

Aminoalkylphosphonic acids				Amino carboxylic acids			
formula	ionic strength	concentration (moles/liter)	V^*_{max}	formula	ionic strength	concentration (moles/liter)	V^*_{max}
$NH_2CH_2PO(OH)_2$	1,2	0,53	0,25	NH_2CH_2COOH	1,2	0,53	2,7
$HOOCCH_2NHCH(CH_3)PO(OH)_2$	0,16	0,0387	3,1	$HOOCH_2CNHCH_2COOH$	0,16	0,0387	9,0
$(HOOCCH_2)_2NCH_2PO(OH)_2$	0,03	0,01	2,1	$(HOOCCH_2)_2NCH_2COOH$	0,03	0,01	4,8
$(HOOCCH_2)_2NC(CH_3)_2PO(OH)_2$	0,03	0,01	2,2				
$(HO)_2OPCH_2NHCH_2CH_2NHCH_2PO(OH)_2$	0,31	0,014	2,1	$HOOCCH_2NHCH_2CH_2NHCH_2COOH$	0,31	0,014	9,0
$(HO)_2OPCH_2 \diagdown NCH_2CH_2N \diagup CH_2PO(OH)_2$ $HOOCCH_2 \diagup \quad \diagdown CH_2COOH$	0,024	0,003	3,7	$(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$	0,024	0,003	4,2

• The value of V_{max} is the mean of the values from several parallel experiments; departures from this value amount to ± 0.1 ml.

(Ethylenebisiminomethylene) diphosphonic Acid (II). The first part of the experiment was as before. Ether was removed from the ether extract, and to the residue (1.95 g of a sirup) we added 10 ml of concentrated hydrochloric acid. The solution was refluxed for seven hours. Hydrochloric acid was vacuum-distilled off until the residue was of constant weight. Water was added to the residue, when a precipitate formed, which was filtered off and crystallized from dilute hydrochloric acid. We obtained 0.7 g (10%); decomp. temp. 276-277°. Found: C 17.0; 16.8; H 6.3; 6.1; P 21.8; 21.7; N 9.5; 9.6; H_2O 12.6%. $C_4H_{18}P_2N_2O_8$. Calculated: C 16.9; H 6.4; P 21.8; N 9.9; H_2O 12.7%. The substance (II) is sparingly soluble in water, but readily soluble in acids and alkalis; it is insoluble in organic solvents; it crystallizes with two molecules of water.

Picrate of O-Tetraethyl (Ethylenebisiminoisopropylidene) diphosphonothioate (III). Acetone (5.8 g, 0.1 mole) was added dropwise to a mixture of 15.4 g (0.1 mole) of diethyl phosphorothioite and 3 g (0.05 mole) of ethylenediamine. The temperature rose to 80°. The reaction mixture was then heated at 85° for 15 minutes, after which it was extracted with ether. The ether extract was dried with sodium sulfate. From the ether solution we prepared the picrate (12 g, yield 26°), decomp. temp. 130°. Found: C 37.4; 37.4; H 5.0; 5.0; P 6.7; 6.7; N 12.7; 12.8; S 6.6; 6.7%. $C_{22}H_{44}P_2N_8S_2O_{18}$. Calculated: C 37.1; H 5.0; P 6.8; N 12.3; S 7.1%.

Picrate of Diethyl (Ethylenebisiminoisopropylidene) bisphenylphosphinate (IV). This was prepared similarly to (III) from 8.75 g (0.05 mole) of diethyl phenylphosphinite, 1.5 g (0.025 mole) of ethylenediamine, and 2.9 g (0.05 mole) of acetone. We obtained 7.5 g (32%) of the picrate, decomp. temp. 152°. Found: C 45.9; 46.0; H 4.6; 4.8; P 6.4; 6.4; N 11.6; 11.7. $C_{36}H_{44}P_2N_8O_{18}$. Calculated: C 46.0; H 4.7; P 6.6; N 11.9%.

When an attempt was made to obtain (ethylenebisiminoisopropylidene)-bisphenylphosphinic acid by hydrolysis of the ester with hydrochloric acid, we isolated a substance of m.p. 80° (from dioxane). Analysis indicated that the substance was phenylphosphonous acid. Found: C 50.6; 50.8; H 4.8; 4.9; P 21.5; 21.6%. $C_6H_7PO_2$. Calculated: C 50.7; H 5.0; P 21.8%.

{Ethylenebis [(carboxymethylimino) methylene]} diphosphonic Acid (V). A mixture of 7.1 g (0.016 mole) of tetrasodium (ethylenebisiminomethylene) diphosphonate and a solution of 2.3 g (0.048 mole) of sodium cyanide in 20 ml of water was prepared in a four-necked flask. With stirring we added 4.3 g (0.048 mole) of a 36% solution of formaldehyde diluted with water to 25 ml; the formaldehyde was added dropwise over 40 hours with gradual raising of the reaction temperature from 20° to

32°. After the addition of each 5 ml of formaldehyde, 5 ml of liquid was vacuum-distilled from the reaction mixture. After the addition of all the formaldehyde the reaction mixture was neutralized with hydrochloric acid, and was then treated with basic lead acetate until completely precipitated. The precipitate of the lead salt was washed with hot water until chloride ions had been removed, and it was then treated with hydrogen sulfide. Lead sulfide was filtered off, and the filtrate was evaporated to dryness on a water bath. Crystallization from water gave 3.6 g (62%) of substance, decomp. temp. 215°. Found: C 26.3; 26.4; H 5.1; 5.2; P 17.4; 16.8; N 7.8; 7.7%. $C_8H_{16}P_2N_2O_{18}$. Calculated: C 26.4 H 5.0; P 17.0; N 7.7%. The substance (V) is readily soluble in water.

(Biscarboxymethylamino) methylphosphonic Acid (VI). This was prepared from 3.2 g (0.02 mole) of disodium aminomethylphosphonate, 3.2 g (0.06 mole) of sodium cyanide, 0.5 g of sodium hydroxide in 15 ml of water, and 6 g (0.06 mole) of 36% formaldehyde solution, as in the synthesis of the substance (V). After neutralization of the reaction mixture and addition of alcohol there was a precipitate. Crystallization from aqueous alcohol gave (VI) (3.2 g, yield 61%), decomp. temp. 208°. Found: C 26.3; 26.0; H 4.5; 4.5; P 13.5; 13.5; N 6.4; 6.4%. $C_5H_{10}PNO_7$. Calculated: C 26.4; H 4.4; P 13.6; N 6.2%. The substance is readily soluble in hot water.

Triethyl 1- (Carboxymethylamino)-1-methylethylphosphonate (VII). 1) By reaction of diethyl 1-amino-1-methylethylphosphonate with ethyl chloroacetate: A mixture of 39 g (0.2 mole) of diethyl 1-amino-1-methylethylphosphonate and 12.2 g (0.1 mole) of ethyl chloroacetate was allowed to stand at room temperature. After several days crystals (diethyl 1-amino-1-methylethylphosphonate hydrochloride) began to separate from the solution. After 40-45 days an excess of ether was added to the mixture, the crystals were separated, and the filtrate was washed with a little water and dried with sodium sulfate. Ether was removed, and vacuum distillation of the residue gave 16.8 g (60%) of (VII); b.p. 77-81° ($3 \cdot 10^{-4}$ mm); n_D^{20} 1.4444; d_4^{20} 1.0810, found MR 69.05; calculated MR 69.10. Found: H 8.7; 8.8; C 47.0; 46.4; P 11.0; 11.2; N 4.9; 5.2%. $C_{11}H_{24}PNO_5$. Calculated: H 8.6; C 46.9; P 11.0; N 5.0%.

2) By reaction of glycine ethyl ester with diethyl phosphite and acetone: Anhydrous glycine ethyl ester prepared by Gavrilov and Akimova's method [8] polymerizes after 2-3 hours. We found that, after three distillations in a stream of nitrogen, glycine ethyl ester [b.p. 42° (6 mm); 52° (10 mm); n_D^{20} 1.4241; d_4^{20} 1.002; found MR 25.74; calculated MR 25.75] does not change in the course of 2-3 days at 0-4° and may be used in the reaction described below.

A mixture of 13.8 g (0.1 mole) of diethyl phosphite, 10.3 g (0.1 mole) of glycine ethyl ester, and 8.7 g (0.15 mole) of acetone was stirred in an atmosphere of nitrogen and gradually heated to 90°. This temperature was maintained for three hours. The reaction mixture was extracted with ten times its volume of ether. The ether solution was added to the sirupy residue and dried with sodium sulfate. Ether was removed, and vacuum distillation of the residue gave 7 g (25%) of substance; b.p. 79-83° ($2 \cdot 10^{-4}$ mm); n_D^{20} 1.4440; d_4^{20} 1.0810; found MR 69.05; calculated MR 69.10.

1-(Carboxymethylamino)-1-methylethylphosphonic Acid (VIII). A mixture of 7 g of triethyl 1-(carboxymethylamino)-1-methylethylphosphonate (VII) and 40 ml of concentrated hydrochloric acid was refluxed for seven hours. The hydrochloric acid was removed, and the residual sirup was decolorized with charcoal and treated with absolute ethanol. The precipitate was recrystallized from water. We obtained 0.8 g (15%) of acid, decomp. temp. 197-198°. Found: C 30.4; 30.3; H 6.1; 6.1; P 15.4; 15.6; N 7.1; 7.3%, $C_5H_{12}NPO_5$. Calculated: C 30.5; H 6.1; P 15.7; N 7.1%.

1-Biscarboxymethylamino-1-methylethylphosphonic Acid (IX). Sodium chloroacetate (23.5 g, 0.2 mole) was added to a solution of 15.7 g (0.1 mole) of 1-amino-1-methylethylphosphonic acid in 25 ml of 8 N NaOH (0.2 mole). The mixture was heated in a boiling water bath, and addition was made of 25 ml of 8 N NaOH (0.2 mole) at such a rate that the pH of the medium was kept at 10-11. The amount of chloride ion was determined on separate test samples. Reaction was complete when the amount of chloride ion reached the calculated value. The reaction mixture was then neutralized, and the acid was isolated as the lead salt, as in the synthesis of (V). After the removal of lead sulfide, the filtrate was concentrated until the residue attained constant weight. The resulting sirup was mixed with absolute alcohol, and gradually a precipitate (5.4 g, yield 20%) separated from the solution. After two recrystallizations from water it had decomp. temp. 150-151°. Found: C 32.7; 32.7; H 5.9; 5.9; P 11.6; 11.7; N 5.4; 5.4%. $C_7H_{14}NPO_7$. Calculated: C 32.9; H 5.5; P 12.1; N 5.5%.

Iminodiacetic acid was synthesized by Chase and Downes's method [7]; decomp. temp. 235°. (Ethylenediimino) diacetic acid was kindly presented by V.G. Yashunskii, to whom the authors express their thanks.

SUMMARY

1. Some (carboxymethylamino) alkylphosphonic acids were synthesized, and it was shown by the chromatographic method that they have complex-forming properties.

2. The complex-forming power of amino phosphonic acids is greater than that of the corresponding amino carboxylic acids.

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ADDITION OF HYDROGEN BROMIDE TO 3,3-DICHLOROPROPENE IN PRESENCE OF BENZOYL PEROXIDE

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Two of the authors of this paper with co-workers showed that the addition of hydrogen bromide to 3,3,3-trichloropropene [1] and to 3,3,3-trichloro-2-methylpropene [2] in presence of benzoyl peroxide proceeds with accompanying rearrangement of a previously unknown type. This rearrangement was interpreted as isomerization of radicals of type (I) into radicals of type (II) in solution:

$$\underset{\text{(I)}}{CCl_3\dot{C}XCH_2Br} \rightarrow \underset{\text{(II)}}{\dot{C}Cl_2CXClCH_2Br},$$

in which X=H or CH_3.

It was shown that an analogous rearrangement of radicals in solution occurs also in the addition of bromine [3] or of bromotrichloromethane [1] to 3,3,3-trichloropropene in presence of benzoyl peroxide. This rearrangement appears to be associated with the fact that radicals of type (II) are more stable than those of type (I). The present work was concerned with the rearrangement in solution of radicals of structure $CHCl_2CHCH_2Br$. For this purpose we investigated the addition of hydrogen bromide to 3,3-dichloropropene in presence of benzoyl peroxide at 60-70°.

In accordance with the reaction scheme for the peroxide effect, the reaction studied should lead to the formation of 3-bromo-1,1-dichloropropane. If the intermediately formed radical (III) is rearranged into the radical (IV).

$$\underset{\text{(III)}}{CHCl_2\dot{C}HCH_2Br} \rightarrow \underset{\text{(IV)}}{\dot{C}HClCHClCH_2Br}$$

the formation of 1-bromo-2,3-dichloropropane may be expected, in accordance with the scheme:

$$Bz_2O_2 \rightarrow C_6H_5^{\cdot}$$

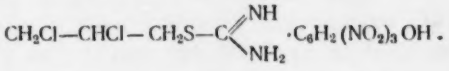
$$C_6H_5^{\cdot} + HBr \rightarrow C_6H_6 + Br^{\cdot}$$

$$CHCl_2CH = CH_2 + Br^{\cdot} \rightarrow CHCl_2\dot{C}H - CH_2Br$$

$$\underset{\text{(III)}}{CHCl_2\dot{C}HCH_2Br} \rightarrow \underset{\text{(IV)}}{\dot{C}HClCHClCH_2Br}$$

$$\dot{C}HClCHClCH_2Br + HBr \rightarrow CH_2ClCHClCH_2Br + Br^{\cdot}.$$

The reaction actually gave a 35% yield of 1-bromo-2,3-dichloropropane together with liquid and solid products of higher molecular weight. The structure of 1-bromo-2,3-dichloropropane was proved by an independent synthesis consisting in the addition of chlorine to allyl bromide in an acid medium. The bromodichloropropanes obtained by the two methods were shown to be identical by examination of the derivatives given with thiourea; mixture melting points were carried out on the picrates of these derivatives, which had the structure:



Severer conditions were required in the reaction with thiourea than in the case of allyl halides (cf. [4]).

The structure of the bromodichloropropane and the fact that the two preparations of this were identical was confirmed also by dehydrohalogenation, which gave the same 1,2-dichloropropene in each case; this was identified as the picrate of the product formed with thiourea, m.p. 170°. If in the reaction of hydrogen bromide with 3,3-dichloropropene some 3-bromo-1,1-dichloropropane had been formed, then in the dehydrohalogenation 3,3-dichloro- and 1,3-dichloro-propenes would also have been obtained.

In this connection we studied the behavior of these dichloropropenes toward thiourea. It was found that 1,3-dichloropropene readily forms a thiopseudourea compound, which was isolated as the picrate, m.p. 195°. 3,3-Dichloropropene reacts with thiourea only under severe conditions and gives a picrate of m.p. 182°. The two picrates both have the composition $C_{10}H_{10}ClN_5O_7S$ and are probably stereoisomers. Mixture tests of these picrates with those obtained from the products of the dehydrohalogenation of the bromodichloropropanes showed depression of melting point. Investigation of all the fractions obtained in the dehydrohalogenation of 3-bromo-1,2-dichloropropane by isolation of the picrates of the thiopseudourea compounds showed that both 3,3-dichloro- and 1,3-dichloro-propenes were absent.

The results show that, in this case also, reaction went with rearrangement and passage of a chlorine atom from the dichloromethyl group to the adjacent carbon atom. The reaction is of interest also from the point of view of the investigation of transformations characteristic of the dichloromethyl group; in heterolytic reactions this group is considerably less reactive than the trichloromethyl group. The results of the present work show that the dichlromethyl group readily enters reactions of the homolytic type.

EXPERIMENTAL

Addition of Hydrogen Bromide to 3,3-Dichloropropene in Presence of Benzoyl Peroxide. A solution of 0.5 g of benzoyl peroxide in 35 g of 3,3-dichloropropene (n_D^{20} 1.4468; d_4^{20} 1.1685) was saturated with a stream of dry bromine-free hydrogen bromide at 60-70°. A white amorphous precipitate gradually formed and was separated at the end of the reaction. The reaction mixture was washed with sodium carbonate solution and with water and was dried over calcium chloride. The reaction products were fractionated through a column at a residual pressure of 28 mm. This gave: Fraction I, b.p. 60-65°, 1.5 g, n_D^{20} 1.5076; Fraction II, b.p. 65-70°, 3.5 g, n_D^{20} 1.5089; Fraction III, b.p. 70-73°, 3.5 g, n_D^{20} 1.5120; Fraction IV, b.p. 73-75°, 21 g, n_D^{20} 1.5171, d_4^{20} 1.7504; residue 15 g.

Fraction IV was redistilled through a column, and a substance (3-bromo-1,2-dichloropropane) was isolated which had the following constants: b.p. 72° (30 mm); n_D^{20} 1.5170; d_4^{20} 1.7488; found MR 33.20. $C_3H_5Cl_2Br$. Calculated MR 33.55. Found: C 18.86; 18.90; H 2.71; 2.76; halogen 77.96; 78.05%. $C_3H_5Cl_2Br_2$. Calculated: C 18.78; H 2.63; halogen 78.60%.

The picrate of 2-(2,3-dichloropropyl)-2-thiopseudourea, m.p. 151°, was prepared. A mixture melting point test with the picrate synthesized by an independent method (see below) showed no depression. Found: C 28.77; 28.78; H 2.55; 2.55%. $C_{10}H_{11}Cl_2N_5O_7S$. Calculated: C 28.86; H. 2.67%.

On analogy with the reaction of hydrogen bromide with 3,3,3-trichloro-2-methylpropene [2] the formation of 3-bromo-1-chloropropene can also be expected. However, investigation of Fractions I-III for the presence of allyl halides (reaction with thiourea under mild conditions and with mercury in sunlight) gave negative results.

Dehydrobromination of 1-Bromo-2,3-dichloropropane. With cooling of the reaction mixture to 0°, a solution of 11.3 g of potassium hydroxide in 50 ml of 2-methoxyethanol was added dropwise to stirred bromodichloropropane (32.3 g) obtained by the addition of hydrogen bromide to 3,3-dichloropropene. The reaction mixture was then washed several times with water and dried over calcium chloride. Distillation from a Favorskii flask gave the following fractions: Fraction I, b.p. 95-100°, 12 g, n_D^{20} 1.4620; and Fraction II, b.p. 100-115°, 1.9 g, n_D^{20} 1.4828.

Fraction I, which contained mainly 2,3-dichloropropene, was redistilled: b.p. 93-94°; n_D^{20} 1.4619; d_4^{20} 1.2193; found MR 25.25. $C_3H_4Cl_2F$. Calculated MR 25.42. The yield of 2,3-dichloropropene was 65%. For 2,3-dichloropropene the literature [5] gives: b.p. 93.8°; d_4^{20} 1.211; n_D^{20} 1.4603. The picrate of 2-(2-chloroallyl)-2-thiopseudourea, m.p. 170.5-171°, was obtained*.

A mixture melting point test with the picrate synthesized by an independent method (see below) showed no depression. Found: C 31.94; 31.82; H 2.89; 2.70; Cl 9.69; 9.66%. $C_{10}H_{10}ClN_5O_7S$. Calculated: C 31.62; H 2.65; Cl 9.34%.

From Fraction II we also obtained only the picrate of 2-(2-chloroallyl)-2-thiopseudourea, m.p. 170°. A mixture with the picrate obtained from Fraction I melted at 170°.

Reaction of 2,2-Dichloropropene and 1,3-Dichloropropene with Thiourea. The reaction between 3,3-dichloropropene (0.4 g) and thiourea (0.5 g) in 5 ml of ethanol was carriedout in a sealed glass tube in a boiling water bath for three hours. The thiopseudourea compound was isolated as the picrate, m.p. 182° (from alcohol). Found: C 31.49; 31.39; H 2.52; 2.61%. $C_{10}H_{10}ClN_5O_7S$. Calculated: C 31.62; H 2.65%. 1,3-Dichloropropene reacts with thiourea under the usual conditions [4]. The picrate obtained melted at 195° (from alcohol) and had a much higher solubility in alcohol than the above-described picrate of m.p. 182°. Found: C 32.01; 31.92; H 2.69; 2.75%. $C_{10}H_{10}ClN_5O_7S$. Calculated: C 31.62; H 2.65%. Mixture tests of these picrates with the picrate obtained from the product of the dehydrobromination of 1-bromo-2,3-dichloropropane showed depression of melting point.

Addition of Chlorine to Allyl Bromide. A stream of chlorine containing hydrogen chloride was passed for 4-5 hours into a solution of 39 g of allyl bromide in 15 ml of hydrochloric acid and 15 ml of diethyl ether. The reaction mixture was then washed with sodium carbonate solution and with water, and it was dried over calcium chloride and distilled through a column at a residual pressure of 25 mm. We obtained Fraction I, b.p. 55-62°, 4.6 g, n_D^{20} 1.5095; Fraction II, b.p. 62-65°, 33.7 g, n_D^{20} 1.5170; Fraction III, b.p. 65-67°, 1.8 g, n_D^{20} 1.5160; residue 12 g. Fractions I and III and the residue were not investigated further.

Fraction II was redistilled through a column, and as a result we obtained 1-bromo-2,3-dichloropropane, which had the following constants: b.p. 75° (33 mm); n_D^{20} 1.5173; d_4^{20} 1.7426; found MR 33.33. $C_3H_5Cl_2Br$. Calculated MR 33.55. Found: C 18.94; 18.97; H 2.61; 2.63%. $C_3H_5Cl_2Br$. Calculated: C 18.78; H 2.63%. The picrate of 2-(2,3-dichloropropyl)-2-thiopseudourea, m.p. 151-152°, was prepared. Found: C 28.26; 28.34; H 2.50; 2.62%. $C_{10}H_{11}Cl_2N_5O_7S$. Calculated: C 28.86; H 2.67%. A dehydrobromination product was obtained from this bromodichloropropane by the action of potassium hydroxide in 2-methoxyethanol, and from this, without any preliminary distillation, the thiopseudourea compound was prepared in the form of its picrate, m.p. 170°. Found: C 31.74; 31.79; H 2.63; 2.69%. $C_{10}H_{10}ClN_5O_7S$. Calculated: C 31.62; H 2.65%.

SUMMARY

When hydrogen bromide reacts with 3,3-dichloropropene in presence of benzoyl peroxide, homolytic rearrangement of radicals occurs ($CHCl_2CHCH_2Br \rightarrow CHClCHCl-CH_2Br$) with formation of 1-bromo-2,3-dichloropropane.

* The substituent in thiopseudourea is described in the original as "2-chloropropenyl-2" and it is assumed that 2-chloroallyl is meant.—Publisher.

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THERMAL TELOMERIZATION OF OLEFINS WITH SILANES

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As previously shown [1-3], olefins undergo thermal telomerization with compounds containing an Si–H bond. The reaction was carried out in steel autoclaves at 260-320° at a high pressure without addition of any initiator or catalyst.

The thermal telomerization of ethylene with trichlorosilane [2], with dichloromethylsilane [1], with dichlorophenylsilane [3], and with triethylsilane [3] has been carried out, as also has that of propene with dichloromethylsilane [1]. The reaction may be represented by the scheme:

$$n > C{=}C < + H{-}SiXYZ \rightarrow H\left[-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-\right]_n SiXYZ,$$

in which X, Y, Z = Cl, CH_3, C_2H_5, C_6H_5.

The thermal telomerization of olefins with silanes appears to be a chain reaction, for it leads to the formation of a mixture of telomer-homologs under conditions under which the lower telomers are unable to react with olefins with formation of higher telomers. As the reaction was carried out in steel autoclaves, there was the suspicion that it may be catalyzed by the walls of the autoclave or initiated by traces of heavy-metal chlorides that could be formed by reaction of the original chlorosilanes with the autoclave walls. To verify these possibilities, we carried out the reaction between ethylene and dichloromethylsilane is a sealed glass tube at 320-240° under a pressure of about 50 atm. The results of this experiment were quite analogous to those obtained when the reaction was carried out under similar conditions, but in an autoclave. In both cases a mixture of telomers was formed. It was thus proved that thermal telomerization can indeed be effected in absence of initiators or catalysts (Table 1). The fact that thermal telomerization is not associated with the formation of traces of heavy-metal halides by the action of the reactants on the autoclave walls was confirmed by the ready and smooth telomerization of triphenylsilane with ethylene in autoclaves. Triphenylsilane is obviously unable to give rise to metal halide impurities. It was shown previously that triethylsilane also gives a mixture of telomers when heated with ethylene in an autoclave under pressure [3].

These results are in accord with the view that thermal telomerization is initiated by dissociation of the silane at the Si–H bond. This view is supported also by the differences that we have observed in the effect of change of reaction conditions between the course of thermal telomerization and that of chemically initiated telomerization of ethylene with carbon tetrachloride or chloroform. Thus, in reactions of the latter type initiated with 2,2'-azobis [2-methylpropionitrile] or with benzoyl peroxide, with rise in temperature the reaction rate increases and the conversion of halomethane falls sharply, which is associated with the rapid consumption of initiator [4-7]. In the thermal telomerization of ethylene with dichloromethylsilane, the conversion of the latter may be raised to high values (80-90%) at all temperatures at which the reaction goes.

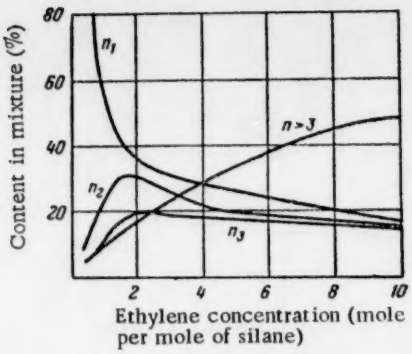


Fig. 1

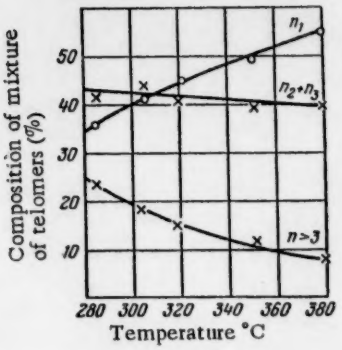


Fig. 2

It is known that the homolytic addition of silanes to substituted ethylenes in presence of peroxides or ultraviolet radiation proceeds in the direction opposite to that required by Markovnikov's rule:

$$RCH{=}CH_2 + H{-}SiX_3 \rightarrow RCH_2CH_2SiX_3.$$

The heterolytic addition of silanes to substituted ethylenes, which is catalyzed by bases, tetrapyridinenickel chloride, and platinum, proceeds in both possible directions [8]:

$$RCH{=}CH_2 + H{-}SiX_3 \rightarrow RCH_2CH_2SiX_3 + \underset{\displaystyle CH_3}{\overset{\displaystyle |}{RCHSiX_3}}.$$

To determine the structure of the addition product formed by dichloromethylsilane and propene under our conditions it was methylated with a Grignard reagent. Investigation of the Raman spectrum of the trimethyl derivative obtained showed that it had the structure $CH_3CH_2CH_2Si(CH_3)_3$. Investigation of the Raman spectrum of the lower fraction showed the absence of isopropyltrimethylsilane.

Hence, like homolytic addition, thermal addition went only in one direction. It is interesting that, like the ethylene reaction [9, 10], the reaction of propene with dichloromethylsilane in presence of platinum proceeds at room temperature; it leads to the formation, in close to the theoretical yield, of dichloromethylpropylsilane, whose structure was also proved by a study of its Raman spectrum.

In the present work we made a more detailed investigation of the effect of change of temperature, pressure, and concentration of olefin on the relative yields of individual telomers, the case taken being the thermal telomerization of ethylene with dichloromethylsilane. Table 2 and Fig. 1 show that the regularities observed previously in the relation between change in telomer composition and increase in ethylene concentration in the initiated telomerization of ethylene with carbon tetrachloride or chloroform [4-6] are preserved in the case of the thermal telomerization of ethylene with dichloromethylsilane. With increase in the amount of ethylene, the content of the lower telomers falls and the content of the higher telomers rises; also, the amount of each component passes through a maximum whose value falls with increase in the number of atoms in the telomer molecule. However, unlike the mixtures of polychloroalkanes, for which the content of the first member of the series (n=1) falls rapidly and amounts to 1-2% at 100-150 atm with 5-10 moles of ethylene per mole of polychloromethane, under these conditions the mixture of alkyldichloromethylsilanes contains 26-18% of dichloroethylmethylsilane.

Table 3 shows that the reaction rate greatly increases with rise in temperature. In 5-10 minutes at 100 atm and 320-350° the conversion attains 60-80%. In these experiments the composition of the mixture of telomers also changes in a regular way: with rise in temperature the content of lower telomers increases and the content of higher telomers decreases (Fig. 2).

TABLE 1

	Expt. in glass	Expt. in autoclave
Molar ratio ethylene/silane	1.8	2.7
Conversion of dichloromethylsilane	46%	46%
Content of dichloroethylmethylsilane in mixture of reaction products	80%	42%
Content of butyldichloromethylsilane in mixture of reaction products	17%	28%

EXPERIMENTAL

Reaction of Ethylene with Dichloromethylsilane in a Sealed Glass Tube. After a 300-ml glass ampoule had been purged with ethylene it was charged with 11.5 g (0.1 mole) of CH_3SiCl_2H. The ampoule was placed in a Dewar vessel containing liquid nitrogen. Ethylene from a gas holder was passed through a drying system and condensed in the ampoule. In all, 4 liters (at 0° and 760 mm) was passed in (4.3 g, 0.18 mole). The ampoule was sealed under reduced pressure and placed in a steel autoclave. Nitrogen was passed into the autoclave up to a pressure of 40 atm. The autoclave was heated at 320-340° for three hours. At this temperature the pressure attained 82 atm and, by calculation, the pressure in the ampoule should have reached 40-50 atm. When the autoclave had cooled, the ampoule was again placed in a Dewar vessel containing liquid nitrogen and opened.

The reaction product was distilled from a flask fitted with a small column. The following fractions were isolated: Fraction I, b.p. 43°, 35 ml; Fraction II, b.p. 50-98°, 1.3 ml; Fraction III, b.p. 98-110°, 4 ml; n_D^{20} 1.4185; d_4^{20} 1.0485; Fraction IV, b.p. 110-145°, 1.1 ml; n_D^{20} 1.0155; Fraction V, b.p. 145-150, 0.3 ml; n_D^{20} 1.4314 d_4^{20} 1.0087.

Fraction I was unchanged dichloromethylsilane. Fractions III, IV, and V consisted mainly of dichloroethylmethylsilane and butyldichloromethylsilane.

The literature [1] gives b.p. 100°, n_D^{20} 1.4180; and d_4^{20} 1.0565 for dichloroethylmethylsilane and b.p. 147-148°, n_D^{20} 1.4310, and d_4^{20} 1.0190 * for butyldichloromethylsilane.

For comparison, an analogous experiment was carried out in a 2700-ml steel autoclave, which was loaded with 1 mole of 1 M CH_3SiCl_2H and 2.7 moles of ethylene. Reaction proceeded at an appreciable rate at 340°, and the pressure then attained 50 atm. Reaction continued for 40 minutes, and 76 g of a mixture of alkyldichloromethylsilanes was obtained. Table 1 gives a comparison of some of the data obtained in the experiments described.

The discrepancy in the yields of the individual telomers in comparable experiments is probably to be attributed to the difference in the molar ratios of ethylene to silane in these experiments.

Thermal Telomerization of Triphenylsilane with Ethylene. A 150-ml autoclave was charged with 32 g of $(C_6H_5)_3SiH$, 30 ml of hexane, and 25 g of ethylene. Heating was for 12 hours at 290-300°. In the course of this time the pressure fell from 100 to 65 atm. We obtained 36.6 g of reaction product, which was vacuum-fractionated from a flask fitted with a small column. We obtained the following fractions: Fraction I, b.p. 155-175° (2.5 mm); 12.6 g; Fraction II, b.p. 150-165° (0.46 mm); 13 g; Fraction III, b.p. 165-180° (0.40 mm); 8 g; residue 4 g.

Fractions I and II rapidly crystallized out, but Fraction III was a slowly crystallizing oil. After crystallization from alcohol, Fraction II had m.p. 68-70°. Found: C 83.48; 82.79; H 7.16; 7.19; Si 9.56; 9.32%. $C_{20}H_{20}Si$. Calculated: C 83.26; H 6.98; Si 9.73%.

* There was a misprint in our previous paper [1]: read d_4^{20} 1.0190 on second line of Table 1, p. 272.

TABLE 2

Expt.	Charge		Composition of mixture of telomers $CH_3SiCl_2(CH_2CH_2)_nH$ (% of sum of all products)			
	CH_3SiCl_2H (moles)	C_2H_4/CH_3SiCl_2H (moles/mole)	$n=1$	$n=2$	$n=3$	$n>3$
1	2	0,75	70	17	8	5
2	5	1,2	57	24	10	9
3	1	1,5	35	31	17	17
4	3	2,8	33	28	19	20
5	2,5	3,4	34	23	19	24
6	1	9	18	17	17	48

TABLE 3

Expt.	Temp. °C	Time (min.)	Conversion of CH_3SiCl_2H (%)	Composition of mixture of telomers (%)			
				$n=1$	$n=2$	$n=3$	$n>3$
1	285	120	44	36	26	15	23
2	305	50	86	41	29	15	15
3	320	10	77	45	30	11	14
4	350	5	60	49	26	13	13
5*	350	—	88	54	27	13	7

*Momentary rise in temperature to above 400°.

Alcohol was distilled from the filtrate, and the residue was combined with Fraction III. The substance was dissolved in petroleum ether, and the solution was subjected to chromatography on alumina. We isolated white crystals, m.p. 81-82°. Found: C 83.52; 82.93; H 7.28; 7.26; Si 8.49; 8.59%. $C_{22}H_{24}Si$. Calculated: C 83.48; H 7.63; Si 8.67%.

As $C_2H_5Si(C_6H_5)_3$ and $C_4H_9Si(C_6H_5)_3$ differ only slightly in composition, the compounds were investigated spectroscopically. Determination of the numbers of methylene and methyl groups by measurement of the intensities of the absorption bands due to C–H valence vibrations in CH_2 and CH_3 groups (2930 and 2965 cm^{-1}) (by method analogous to that described previously [11]) showed that these compounds had the proposed structures.

The residue, insoluble in alcohol and petroleum ether, was extracted with boiling benzene, recrystallized from benzene, and sublimed. This gave long needles of m.p. 224° (in copper block). For $(C_6H_5)_3SiOSi(C_6H_5)_3$ [12]; gives m.p. 221°. Found: C 80.90; 80.90; H 5.65; 5.66; Si 10.31; 10.60%. $C_{36}H_{30}Si_2O$. Calculated: C 80.81; H 5.65; Si 10.60%.

Reactions of Propene with Dichloromethylsilane

Addition of Dichloromethylsilane to Propene in Presence of Chloroplatinic Acid. A cooled 500-ml steel autoclave was charged with 65 g of CH_3SiCl_2H, 50 ml of propene, and 0.1 ml of a solution of 0.00865 g of H_2PtCl_6 in isopropyl alcohol. Reaction started when room temperature was reached and proceeded with appreciable evolution of heat. After one hour the reaction product was discharged from the autoclave and fractionated through a column. We obtained 77 g of a fraction of b.p. 123-124°; n_D^{20} 1.4230; d_4^{20} 1.0432; found MR 38.34. $C_4H_{10}SiCl_2$. Calculated MR 38.64. No other fractions boiling in this region were found.

Raman spectrum of fraction of b.p. 123-124°:

$\Delta\nu$ (cm^{-1}): 169 (1b), 186 (0b), 217 (3v.b), 240 (2), 287 (ob), 344 (2p), 354 (2), 419 (0), 476 (10b), 537 (0), 651 (0), 695 (3), 745 (1b), 799 (1), 820 (0), 895 (2), 1029 (3), 1067 (1), 1103 (1), 1147 (0), 1202 (3), 1238 (0), 1261 (1), 1298 (2), 1350 (0), 1402 (5), 1449 (5), 2870 (9), 2901 (10), 2933 (4), 2968 (8b).

The Raman spectrum of this substance is completely identical with that of $CH_3SiCl_2C_3H_7$-n.

Thermal Telomerization of Propene with Dichloromethylsilane. The reaction product, obtained as we described previously [1], was fractionated through a column. From 369 g of product we isolated the following fractions:

Fraction I, b.p. 40-50°; 75 g; Fraction II, b.p. 50-110°; 43 g; Fraction III, b.p. 110-130°, 156 g; Fraction IV, b.p. 56-75° (30 mm); 15 g; Fraction V, b.p. 75-90° (30 mm); 28 g.

Fraction III was methylated with a Grignard reagent. The product was fractionated through a column, and the following fractions were collected:

Fraction I, b.p. 86-88.5°; n_D^{20} 1.3900; d_4^{20} 0.7063; 7 g; Fraction II, b.p. 88.5-89°; n_D^{20} 1.3925; d_4^{20} 0.7020; 83g.

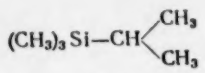
For $(CH_3)_3SiC_3H_7$-n [13] gives: n_D^{20} 1.3929; d_4^{20} 0.7020.

The Raman spectra of Fractions I and II were completely identical and corresponded to the structure $(CH_3)_3Si-CH_2-CH_2-CH_3$ [14].

Raman spectrum of Fraction I ($\Delta\nu$ in cm^{-1})

202 (4b), 223 (2b), 292 (1), 348 (3), 570 (3), 604 (10), 690 (7b), 839 (2b), 1028 (3), 1062 (2), 1196 (3b), 1250 (2b), 1407 (5), 1446 (5), 2870 (9), 2901 (10), 2933 (4), 2968 (8b).

No lines corresponding to



[15]

were detected. As the Raman spectrum of Fraction II was completely identical with that given above, we do not give it here*.

Fraction V was methylated by the Grignard reaction. We obtained $C_6H_{13}Si(CH_3)_3$; b.p. 82-83° (60 mm); n_D^{20} 1.4171; d_4^{20} 0.7493; found MR 53.15; calculated MR 53.45. Found: C 68.13; 68.00; H 14.06; 13.99; Si 17.79; 17.75%. $C_9H_{22}Si$. Calculated C 68.20; H 14.00; Si 17.72%.

Investigation of the Effect of Conditions on the Yields of Telomers

The experiments were carried out in shaking autoclaves provided with powerful electric heaters to enable the required temperature to be reached quickly and with water jackets to permit rapid cooling. In other respects the experimental procedure was as described previously [1-4, 7]. Table 2 gives a summary of experiments carried out with the object of determining the effect of ethylene concentration on the composition of the mixture of telomers. The pressure was 150 ± 5 atm, the temperature was 300 ± 10°, and the volume of the autoclave was 500 or 2700 ml, depending on the amount of dichloromethylsilane used. In these experiments we attempted to attain approximately the same conversion of dichloromethylsilane (40-60%). The reaction time was 0.5-2 hours.

Fig. 1. gives a graphical representation of the relation of the composition of the mixture of telomers to the ethylene concentration.

Table 3 refers to experiments in a 350-ml autoclave with exact control of temperature. The pressure was 100 ± 5 atm. The charge of dichloromethylsilane was 0.5 mole. In all experiments 2 moles of ethylene was taken per mole of silane.

From a comparison of Experiments 1 and 2 (Table 3) with Experiments 3 and 4 (Table 2) and the experiment at 50 atm it will be seen that change in pressure in the range 50-150 atm (other conditions being approximately equal) has little effect on the composition of the mixture of telomers.

* Infrared and Raman spectra were determined at the Institute of Organic Chemistry, Academy of Sciences of the USSR. We express our sincere thanks to L.A. Leites for the spectrographic determinations.

SUMMARY

1. Thermal telomerization, previously found to occur between ethylene and dichloromethylsilane and other silanes, has now been carried out with triphenylsilane. Ethyl- and butyl-triphenylsilanes were isolated.

2. Under the conditions for the telomerization of propene with dichloromethylsilane, addition occurred in the direction opposite to that required by Markovnikov's rule, as also in the case of homolytic addition to propene.

3. Thermal-telomerization reactions of the type studied proceed in the same way in glass and in steel, so that they are not catalyzed by the walls of the autoclave or by metal salts formed at the walls.

4. A study was made of the effects of temperature, relative amounts of reactants, and pressure on the yields of individual telomers and on the conversion of dichloromethylsilane.

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SYNTHESIS OF ORGANOMERCURY NITRO COMPOUNDS

COMMUNICATION 2. MERCURATION OF ALIPHATIC COMPOUNDS CONTAINING A MOBILE HYDROGEN ATOM WITH THE MERCURY SALT OF TRINITROMETHANE

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In the preceding communication [1] we described the synthesis of organomercury nitro compounds of the aromatic and heterocyclic series with the aid of a new mercurating agent, the mercury salt of trinitromethane:

$$ArH + Hg[C(NO_2)_3]_2 \rightarrow ArHgC(NO_2)_3 + HC(NO_2)_3.$$

It was found that the (trinitromethylmercuri) arenes formed in this reaction may exist in two tautomeric forms

$$RHgC(NO_2)_3 \rightleftarrows RHgO{-}{-}N{=}C(NO_2)_2$$
$$\downarrow$$
$$O$$

and that, in the crystalline state, they are true organometallic compounds.

We considered it to be of interest to study the action of the mercury salt of trinitromethane on aliphatic compounds. It is known [2] that aliphatic compounds containing a mobile hydrogen atom are readily mercurated by various mercuric salts. However, simultaneously there often occurs either change in the functional group of the compound to be mercurated or the formation of polymercurated products. We found that, by use of the mercury salt of trinitromethane as mercurating agent, aliphatic compounds containing a mobile hydrogen atom are smoothly mercurated with formation of substances of general formula $R{-}Hg{-}C(NO_2)_3$:

$$RH + Hg[C(NO_2)_3]_2 \rightarrow RHgC(NO_2)_3 + HC(NO_2)_3.$$

We made a detailed study of this reaction for the cases of malonic ester, acetoacetic ester, nitroacetic ester, 2,4-pentanedione (acetylacetone), acetone, and cyclopentanone. Mercuration was carried out in water or in moist ether at room temperature. The yields of the corresponding monomercurated compounds were 55-95%. When the reaction was carried out in water, the yields of products attained the theoretical amounts, whereas in ether they did not exceed 60%. After removal of solvent, the mercuration products were carefully washed with water until free from the mercury salt of trinitromethane and from free trinitromethane liberated during the reaction.

In no case was the formation of polymercurated compounds or change in the functional groups observed. The monomercurated compounds obtained were readily soluble in alcohol, acetone, and ether, but were insoluble in water; they had chemical properties characteristic for organomercury compounds containing a mobile

mercury atom. Thus, dilute hydrochloric acid breaks down the organomercury nitro compounds which we synthesized with formation of the original organic substance and trinitromethane, e.g.,

$$(NO_2)_3CHgCH_2COCH_3 + 2HCl \rightarrow (NO_2)_3CH + HgCl_2 + CH_3COCH_3.$$

Under the action of bromide, smooth replacement of the mercury atom by bromine occurs with formation of the bromo derivative of the aliphatic compound, mercuric bromide, and bromotrinitromethane:

$$(NO_2)_3CHgCH_2COCH_3 + 2Br_2 \rightarrow (NO_2)_3CBr + HgBr_2 + BrCH_2COCH_3.$$

EXPERIMENTAL

Reaction of the Mercury Salt of Trinitromethane with Malonic Ester

$$ROOCCH_2COOR + Hg[C(NO_2)_3]_2 \longrightarrow ROOCCH(HgC(NO_2)_3)COOR + HC(NO_2)_3.$$

To a solution of 1 g (0.002 mole) of the mercury salt of trinitromethane in 12 ml of ether, 1.15 g (0.007 mole) of malonic ester was added; the reaction mixture was left for 12 hours at room temperature. After evaporation of the ether, crystals separated, and were washed with water, dried, and then recrystallized from carbon tetrachloride; decomp. temp. above 250°; yield 0.35 g (35%). Found: C 18.84; 18.71; H 2.49; 2.29; N 7.97; 8.01%. $C_8H_{11}N_3O_{10}Hg$. Calculated: C 18.85; H 2.18; N 8.24%.

The product is readily soluble in benzene, toluene, acetone, and ethyl acetate, but is insoluble in water, hexane, and cyclohexane.

Reaction of the Mercury Salt of Trinitromethane with Acetoacetic Ester

$$CH_3COCH_2COOR + Hg[C(NO_2)_3]_2 \longrightarrow CH_3COCH(HgC(NO_2)_3)COOR + HC(NO_2)_3.$$

The mercuration of acetoacetic ester with the mercury salt of trinitromethane was carried out in the same way as the mercuration of malonic ester. The mercuration product was a white crystalline substance; it was recrystallized from carbon tetrachloride or benzene; m.p. 159° (decomp.); yield 62%. Found: C 17.73; 17.86; H 2.02; 1.93; N 8.59; 8.59%. $C_7H_9O_9N_3Hg$. Calculated: C 17.52; H 1.89; N 8.76.

When this reaction was carried out in an aqueous solution of the mercury salt of trinitromethane, the yield of the same mercuration product attained 80%. Trinitromethane (20 g, 0.13 mole) in 5 ml of water was added with stirring to mercuric oxide (16 g, 0.07 mole) in 20 ml of water; the temperature rose to 30°. The contents of the flask were stirred for 30 minutes at room temperature, and 26.6 g (0.20 mole) of acetoacetic ester was added to the resulting aqueous solution of the mercury salt of trinitromethane. The reaction mixture was left for 10-12 hours at room temperature. The crystals that separated were filtered off, washed several times with water until the washings were colorless, and dried in air; m.p. 159°. The product was soluble in dichloroethane, alcohol, and acetone, but was insoluble in water and petroleum ether. Treatment with dilute hydrochloric acid gave the original acetoacetic ester, which was characterized as its 2,4-dinitrophenylhydrazone, m.p. 96°. The literature [3] gives m.p. 96°.

Reaction of the Mercury Salt of Trinitromethane with 2,4-Pentanedione

$$CH_3COCH_2COCH_3 + Hg[C(NO_2)_3]_2 \longrightarrow CH_3COCH(HgC(NO_2)_3)COCH_3 + HC(NO_2)_3.$$

2,4-Pentanedione is mercurated with the mercury salt of trinitromethane under the same conditions as the mercuration of malonic and acetoacetic esters. The 2,4-pentanedione mercuration product was recrystallized from dichloroethane; m.p. 158° (decomp.); yield 95%. Found: C 15.98; 16.23; H 1.62; 1.55; N 8.94; 8.92%. $C_6H_7O_8N_3Hg$. Calculated: C 16.02; H 1.57; N 9.34%.

Treatment of the mercuration product with dilute hydrochloric acid gave 2,4-pentanedione, mercuric chloride, and trinitromethane. The 2,4-pentanedione was characterized as its 2,4-dinitrophenylhydrazone, m.p. 209°. The literature [4] gives m.p. 209°.

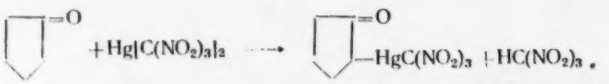
Reaction of the Mercury Salt of Trinitromethane with Acetone

$$CH_3COCH_3 + Hg[C(NO_2)_3]_2 \longrightarrow CH_3COCH_2HgC(NO_2)_3 + HC(NO_2)_3$$

Unlike the mercuration of malonic ester, acetoacetic ester, and 2,4-pentanedione, the reaction of the mercury salt of trinitromethane with acetone required 70 hours for its completion when the reaction was carried out in ether and 50 hours when water was used as solvent. (Trinitromethylmercuri) acetone was recrystallized from dichloroethane; m.p. 153°; the yield was quantitative. Treatment of (trinitromethylmercuri) acetone with dilute hydrochloric acid gave acetone, mercuric chloride, and trinitromethane. The acetone was characterized as its 2,4-dinitrophenylhydrazone, m.p. 126°. The literature [4] gives m.p. 126°. Treatment of (trinitromethylmercuri) acetone with bromine gave bromoacetone, bromotrinitromethane, and mercuric bromide.

A chloroform solution of bromine was added to a chloroform solution of 4 g of (trinitromethylmercuri) acetone until the color of bromine persisted. The mercuric bromide that then separated was filtered off, washed with chloroform, and weighed; yield 3.4 g (94.5%). Distillation of the chloroform solution through a column gave 1.2 g (85.5%) of bromoacetone, b.p. 40-42° (13 mm), and 2 g (87%) of bromotrinitromethane, b.p. 58° (13 mm) and n_D^{20} 1.4899. For bromoacetone the literature [5] gives b.p. 40-42° (13 mm), and for bromotrinitromethane it gives [6] b.p. 63° (14 mm) and n_D^{20} 1.4900.

Reaction of the Mercury Salt of Trinitromethane with Cyclopentanone



The mercuration of cyclopentanone with the mercury salt of trinitromethane was carried out in water over a period of five days. The precipitate formed was filtered off, washed with water, dried in air, and recrystallized from dichloroethane; m.p. 140° (decomp.); the yield was quantitative. Found: C 16.70; 16.57; H 1.77; 1.73; N 9.55; 9.62%. $C_6H_7O_7N_3Hg$. Calculated: C 16.61; H 1.63; N 9.69%.

Treatment of the mercuration product from cyclopentanone with dilute hydrochloric acid gave cyclopentanone, mercuric chloride, and trinitromethane; the 2,4-dinitrophenylhydrazone of cyclopentanone had m.p. 146°. The literature [4] gives m.p. 146°.

Reaction of the Mercury Salt of Trinitromethane with Nitroacetic Ester

$$NO_2CH_2COOR + Hg[C(NO_2)_3]_2 \longrightarrow \underset{\displaystyle HgC(NO_2)_3}{\underset{|}{NO_2CHCOOR}} + HC(NO_2)_3.$$

Mercuration of nitroacetic ester with the mercury salt of trinitromethane (equimolecular amounts of reactants were taken) in water was complete in 15 minutes and gave a quantitative yield; m.p. 134-135°. Found: C 12.38; 12.33; H 1.22; 1.38; N 11.27; 11.19%. $C_5H_6O_{10}N_4Hg$. Calculated: C 12.44; H 1.25; N 11.60%.

SUMMARY

1. The mercury salt of trinitromethane readily mercurates aliphatic compounds containing a mobile hydrogen atom without any effect on the functional groups of the aliphatic compounds. The formation of polymercurated products is not observed.

2. Mercuration of the aliphatic compounds studied with the mercury salt of trinitromethane proceeds in the cold in an aqueous medium in good yield.

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SYNTHESIS OF UNSATURATED NITRO COMPOUNDS WITH THE AID OF TRIPHENYLPHOSPHINE

COMMUNICATION 1. REACTION OF METHYL (TRIPHENYLPHOSPHORANYLIDENE) ACETATE WITH AROMATIC NITRO ALDEHYDES

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In 1919-20 Staudinger and Meyer [1] described the preparation of the phenylimine of diphenylketene from (diphenylmethylene) triphenylphosphorane and phenyl isocyanate by heating a mixture of them in benzene. They considered that the reaction can be expressed by the scheme:

$$(C_6H_5)_3P=C(C_6H_5)_2 + C_6H_5NCO \rightarrow (C_6H_5)_3P(O)-C(C_6H_5)_2-C(O)=NC_6H_5 \longrightarrow$$
$$\rightarrow (C_6H_5)_2C=C=NC_6H_5 + (C_6H_5)_3PO.$$

A little later Luscher [2] carried out the reaction of (diphenylmethylene) triphenylphosphorane with diphenylketene and obtained tetraphenylallene:

$$(C_6H_5)_3P=C(C_6H_5)_2 + (C_6H_5)_2C=C=O \xrightarrow[C_6H_6]{140^\circ,\ 2\ \text{hours}} (C_6H_5)_2C=C=C(C_6H_5)_2 + (C_6H_5)_3PO.$$

From 1953 onward there appeared a series of papers by Wittig [3, 4] in which methylenephosphoranes were used as reagents for the introduction of a double bond into various organic compounds:

$$(C_6H_5)_3P + XCH_2R \rightarrow (C_6H_5)_3P\cdot XCH_2R \xrightarrow{-HX} (C_6H_5)_3P=CHR$$
$$X=Cl, Br$$
$$(C_6H_5)_3P=CHR + R'COR'' \longrightarrow \cdot \begin{matrix} R' \\ R'' \end{matrix} \!\!> C=CHR + (C_6H_5)_3PO.$$

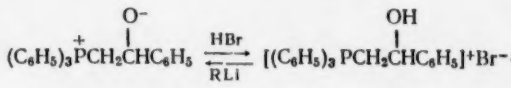
Taking the reaction between methylenetriphenylphosphorane as their example, Wittig and Schöllkopf [4] proposed the following mechanism for this peculiar reaction: the betaine analog is first formed,

$$(C_6H_5)_3P=CH_2 + (C_6H_5)_2CO \rightarrow (C_6H_5)_3\overset{+}{P}CH_2\overset{O^-}{C}(C_6H_5)_2$$

and this, as a result of the tendency for phosphorus to form a decet, is converted into an intermediary having a four-membered ring:

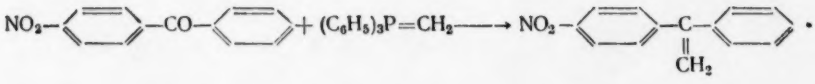
This decomposes into triphenylphosphine oxide and 1,1-diphenylethylene:

The formation of betaine analogs in this reaction was confirmed by the formation of a crystalline salt by treatment of the "betaine" (arising in the reaction between methylenetriphenylphosphorane and benzaldehyde) with HBr and the reverse transformation of this salt into the original betain when treated with RLi:

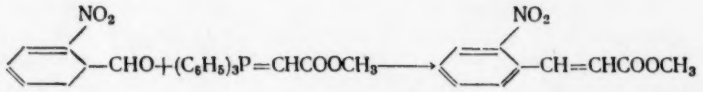


This reaction is remarkable in that the corresponding unsaturated compounds can be prepared from many aldehydes and ketones without any effect on other functional groups. This reaction interested us because of the possibility of preparing unsaturated nitro compounds in this way.

Only one example of such a reaction is given in the previous papers on this subject: the preparation of 1-p-nitrophenyl-1-phenylethylene from 4-nitrobenzophenone and methylenetriphenylphosphorane [4]:



In the present paper we describe the reaction of some aromatic nitro aldehydes with methyl (triphenylphosphoranylidene) acetate $(C_6H_5)_3P=CHCOOCH_3$ (I). We carried out the reaction of methyl(triphenylphosphoranylidene) acetate with o-nitrobenzaldehyde, m-nitrobenzaldehyde, p-nitrobenzaldehyde, o-nitrocinnamaldehyde, and 2,4,6-trinitrobenzaldehyde:



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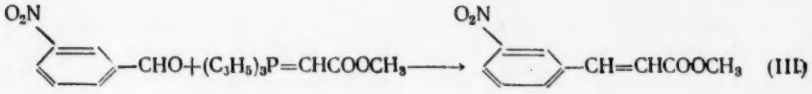

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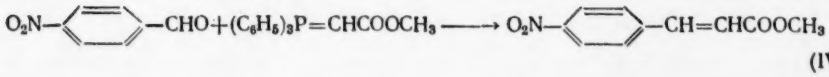
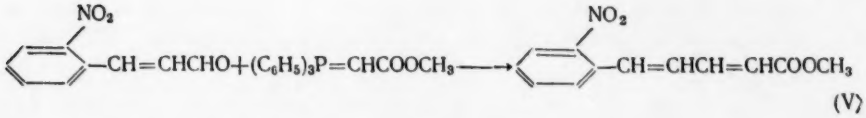
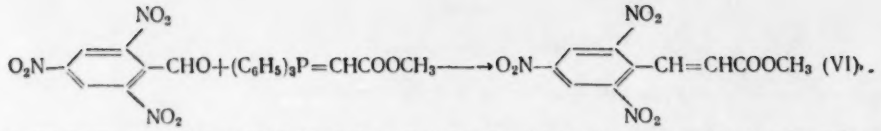


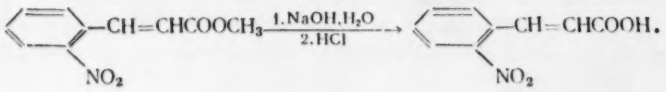
(IV)



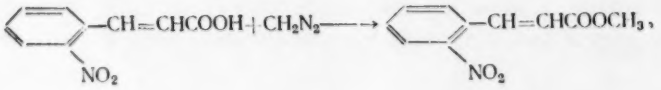
(V)



The reaction was carried out by boiling the reactants together in benzene under an atmosphere of nitrogen for several hours. In all cases the methyl esters of the corresponding α, β-unsaturated acids were isolated. To determine the configuration of the nitrocinnamic acids obtained, the methyl o-nitrocinnamate synthesized was hydrolyzed under very mild conditions with aqueous-methanolic sodium hydroxide:



From the reaction mixture we isolated only trans-o-nitrocinnamic acid, i.e., in this case (as, incidentally, in all methods for the preparation of cinnamic acids from the corresponding benzaldehydes), the reaction proceeds in a stereospecific manner with formation of the trans configuration. The possibility of change of configuration during hydrolysis was excluded by conversion of the acid into the original methyl ester:



EXPERIMENTAL

Methyl (triphenylphosphoranylidene) acetate (I) was prepared by the method described by Isler and coworkers [5]. Its reaction with aldehydes was carried out in a round-bottomed three-necked flask fitted with reflux condenser, mechanical stirrer with a glycerol seal, and a tube for the passage of gas (N_2).

Preparation of Methyl o-Nitrocinnamate (II). A mixture of 7.5 g of o-nitrobenzaldehyde, 22.5 g of (I), and 250 ml of dry benzene was boiled with stirring for four hours in a stream of nitrogen. Benzene was vacuum-distilled off, and the residue was extracted with ether. Ether was distilled off, and there remained 16 g of a mixture of reaction product, (I), and $(C_6H_5)_3PO$ (most of the $(C_6H_5)_3PO$ remained in the residue from the ether extraction because it is sparingly soluble in ether), which was crystallized from aqueous alcohol; this gave 7.6 g of methyl o-nitrocinnamate, m.p. 70-72°. The literature [6] gives m.p. 72-73°.

Hydrolysis of the Methyl Ester (II). The ester (II) (4.3 g) was added to a water-cooled solution of 2 g of sodium hydroxide in 2 ml of water and 50 ml of methanol. The mixture was left at room temperature for five days. The precipitate (2.2 g of Na salt) was filtered off; excess of carbon dioxide was passed through the solution, and filtration gave Precipitate A; the filtrate was evaporated to give Precipitate B. The Na salt and Precipitates A and B (0.3 g did not dissolve) were dissolved in water, and excess of 5% sulfuric acid was added; the precipitates were washed with water and dried in air; this gave 3.4 g of o-nitrocinnamic acid, m.p. 240° (i.e., trans-o-cinnamic acid). The literature [7] gives m.p. 240°.

Reaction of trans-o-Nitrocinnamic Acid with Diazomethane. A solution of diazomethane (from 3 g of methylnitrosourea and 10 ml of 40% aqueous potassium hydroxide) in 40 ml of ether was added gradually to a cooled (ice water) suspension of 2.6 g of the acid in 120 ml of dry acetone; the mixture became homogeneous. Solvents were distilled off, and we obtained 2.9 g of methyl o-nitrocinnamate, m.p. 71-72°, undepressed by admixture of the original methyl ester (II).

Preparation of Methyl m-Nitrocinnamate (III). A stirred mixture of 4.5 g of m-nitrobenzaldehyde, 10 g of (I), and 50 ml of dry benzene was boiled for ten hours in a stream of nitrogen. When the solution was cooled, large clear yellowish crystals (0.55 g) of the methyl ester (III), m.p. 122-124°, separated. Benzene was distilled off, and the residue was subjected to continuous hot extraction with ether for eight hours. There was a precipitate

of 8.2 g of crystals from the extract, and removal of ether left a further 4.8 g of crystals; the crystals were combined and crystalized from alcohol; this gave 4.25 g of the methyl ester (III), m.p. 123-124°; in all, 4.8 of (III) was obtained. The literature [8] gives m.p. 123-124°.

Preparation of Methyl p-Nitrocinnamate (IV). A stirred mixture of 4.6 g of p-nitrobenzladehyde, 10 g of (I), and 50 ml of dry benzene was boiled for six hours in a stream of nitrogen. The mixture was left overnight and filtered; this gave 4.3 g of the methyl ester (IV), m.p. 161-162° (from alcohol). The benzene solution was evaporated, and crystallization of the residue from alcohol gave a further 1.2 g of the methyl ester (IV), m.p. 160-161°; in all, we obtained 5.5 g of the methyl ester (IV). The literature [8] gives m.p. 160°.

Preparation of Methyl 5-o-Nitrophenyl-2,4-pentadienoate (V). A stirred mixture of 5.4 g of o-nitrocinnamaldehyde, 10 g of (I), and 50 ml of dry benzene was boiled for six hours in a stream of nitrogen. When the solution cooled we obtained 2.5 g of the methyl ester (V), m.p. 108-110°. The benzene solution was evaporated, and the residue (A) was extracted with ether; from the ether we obtained 4.7 g of crystals, which were recrystallized from alcohol; this gave 1.8 g of the methyl ester (V), m.p. 108-110°. The ether-insoluble part of A was subjected to continuous hot extraction with ether for six hours, and 3.3 g of $(C_6H_5)_3PO$, was precipitated from the extract; from the ether we obtained 2 g of crystals, and recrystallization of these from alcohol gave 0.7 g of the methyl ester (V), m.p. 109-110°. In all, we obtained 5 g of the methyl ester (V), m.p. 110-111° (from absolute alcohol). Found: C 61.70; 61.58; H 4.80; 4.85; N 6.08; 6.13%. $C_{12}H_{11}NO_4$. Calculated: C 61.79; H 4.72; N 6.01%.

Preparation of Methyl 2,4,6-trinitrocinnamate (VI). The reaction mixture obtained by boiling a mixture of 7.5 g of 2,4,6-trinitrobenzaldehyde, 10 g of (I), and 100 ml of dry benzene for ten hours in a stream of nitrogen was evarporated to dryness. The residue was extracted with ether; from the ether we obtained 5.7 g of crystals. The undissolved residue from the first extraction was subjected to continuous hot extraction with ether for 4-6 hours; from the ether we obtained 9.8 g of crystals. Each portion of crystals (5.7 g and 9.8 g) was recrystallized from alcohol and gave 3.1 g and 3.4 g, respectively, of the methyl ester (VI), i.e., in all we obtained 6.5 g of the methyl ester (VI), m.p. 82-84° (from absolute alcohol). Found: C 40.69; 40.78; H 2.51; 2.46; N 13.99; 13.74%. $C_{10}H_7N_3O_8$. Calculated: C 40.40; H 2.36; N 14.14%.

SUMMARY

1. A study was made of the reaction of $(C_6H_5)_3P{=}CHCOOCH_3$ with nitro aldehydes, and the methyl esters were prepared of o-, m-, and p-nitrocinnamic acids, 2,4,6-trinitrocinnamic acid, and 5-o-nitrophenyl-2,4-pentadienoic acid.

2. On the assumption that the preparation of methyl o-nitrocinnamate can be taken as typical it was shown that the reaction proceeds stereospecifically with formation of the trans form.

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FLUORINE-CONTAINING β-LACTONES

COMMUNICATION 1. β,β-BISTRIFLUOROMETHYL-β-PROPIOLACTONE AND ITS PROPERTIES

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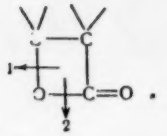
β-Lactones, which contain a strained four-membered ring, are unstable, extremely reactive compounds. They have properties determined by their ring-opening reactions; these may take two different courses: 1) with rupture of the bond between oxygen and carbon, and 2) with rupture of the bond between oxygen and the carbonyl group:

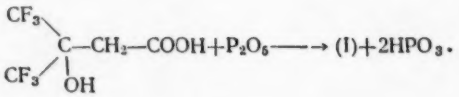


The course taken depends largely on the nature of the lactone, the character of the attacking reagent, and the reaction conditions. In this connection it was of interest to study the chemical properties of the previously unknown fluorine-containing β-lactones.

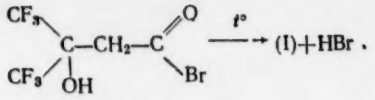
A study of the properties of β,β-bistrifluoromethyl-β-propiolactone [4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid β-lactone] formed the subject of the present investigation.

One of the most widely used methods for the preparation of β-lactones is the condensation of a ketene with a carbonyl compound [1]. It was found that perfluoroacetone reacts with ketene very much more readily than acetone does; reaction occurs under strong cooling in absence of catalyst, and it gives β,β-bistrifluoromethyl-β-propiolactone (I) in quantitative yield:

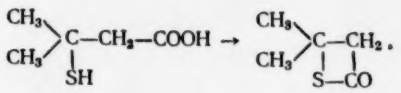
Quite unexpectedly, the lactone (I) was obtained also in the dehydration of 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid with phosphoric oxide:



The lactonization of 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyryl bromide occurs still more easily (simple distillation):

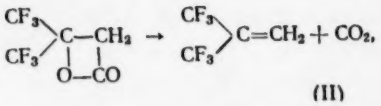


This unusual case of previously unknown ready lactonization of a β-hydroxy acid or its acid bromide* may be explained by the induction effect of two trifluoromethyl groups, which confers a certain mobility on the hydrogen atom of the hydroxy group (esters and amides of 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid are soluble in dilute alkalis). The known analogous ready lactonization of 3-mercapto-3-methylbutyric acid into β,β-dimethyl-β-propiothiolactone is probably to be explained analogously by the high mobility of the hydrogen of the thiol group, as compared with that of hydrogen in hydroxyl [2]:



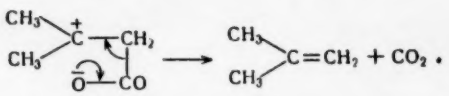
Lactonization is favored also by the fact that the trifluoromethyl groups greatly strengthen the link between the tertiary carbon and oxygen, which completely excludes the competing dehydration into the α,β-unsaturated compound that is of predominant significance in the case of nonfluorinated β-hydroxy acids [3].

The lactone (I) undergoes thermal decomposition into carbon dioxide and 3,3,3-trifluoro-2-(trifluoromethyl) propene (II) only when heated to 340-350°

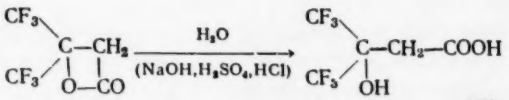


(II)

whereas β-isovalerolactone decomposes when heated to only 60° [9]. β-Isovalerolactone decomposes in the same way when dissolved in water at room temperature, evidently because the methyl groups screen the tertiary carbon atom to a certain extent and render the stabilization of the ion formed in a polar solvent by the elimination of carbon dioxide more probable than its stablization by the addition of the elements of water:



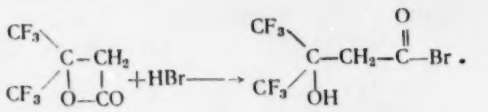
Unlike β-isovalerolactone, β,β-bistrifluoromethyl-β-propiolactone reacts with water only after prolonged heating, when it gives 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid (III). The same acid is obtained when the lactone is decyclized with alkali or concentrated sulfuric or hydrochloric acid:



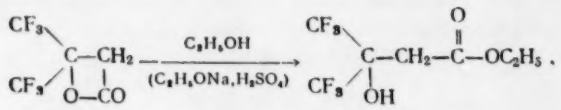
(III).

*Data in the literature on the cyclization of β-hydroxy α,α-dicarboxylic acids to lactones were rejected in the later work of Davidson and Bernhard [4] and Hurd and Hayao [5]. The suggestion of the intermediate formation of a β-lactone from β-hydroxy-β-t-butylhydrocinnamic acid [6] also appears to be improbable in view of modern views of the mechanism of the spontaneous decomposition of salts of β-halo acids [7, 8].

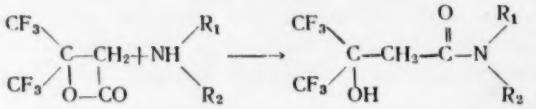
When treated with anhydrous hydrogen bromide, the lactone (I) gives 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyryl bromide (IV):



With alcohol the lactone (I), in absence of catalyst and also in presence of acids or alkalis, gives only one product, ethyl 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyrate (V):



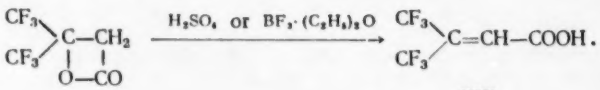
With ammonia or a primary or secondary amine, even under conditions that most favor the formation of amino acids, only the corresponding hydroxy amides (VI–X) are obtained:



(VI) R_1,R_2—H; (VIII) R_1—H; R_2—C_2H_5; (X) R_1,R_2—$(CH_2)_5$—
(VII) R_1,R_2—CH_3; (IX) R_1—H; R_2—C_6H_5.

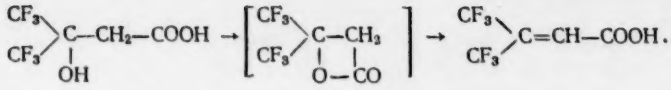
Hence, the outstanding feature of β,β-bistrifluoromethyl-β-propiolactone is the great strength of the bond between oxygen and tertiary carbon, which determines its exceptional stability and the fact that all decyclizations proceed in the direction of derivatives of 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid.

Tertiary amines, and also sodium or traces of caustic alkali, cause the lactone to polymerize to a clear solid or semisolid polymer, which softens at 30-40° and is a 4,4,4-trifluoro-3-(trifluoromethyl) crotonic polyester of low molecular weight. Hydrolysis of the polyester with alkali leads to the acid (III), but treatment with anhydrous sulfuric acid or pyrolysis leads to 4,4,4-trifluoro-3-(trifluoromethyl) crotonic acid (XI). The acid (XI) is obtained in good yield by the isomerization of the lactone under the action of anhydrous sulfuric acid or the ether complex of boron trifluoride:



(XI)

By the dehydration of 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl)-butyric acid with concentrated sulfuric acid, 4,4,4-trifluoro-3-(trifluoromethyl) crotonic acid was again obtained. This was unexpected in view of the fact that we were unable to dehydrate the ethyl ester of this hydroxy acid even under severe conditions [10]. Consideration of these data in conjunction with the fact of the ready formation of the lactone (I) from 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid under the action of phosphoric oxide enables us to suggest that under the action of anhydrous sulfuric acid the first act is the formation of the β-lactone, which is not isolated because of its isomerization under these conditions to 4,4,4-trifluoro-3-(trifluoromethyl) crotonic acid:



EXPERIMENTAL

Anhydrous Perfluoroacetone

Perfluoroacetone hydrate forms very hygroscopic white crystals which melt at about 40°. However, the "hydrate" obtained by the oxidation of perfluoroisobutene by Morse's method [11] was a colorless liquid and, apart from perfluoroacetone and water, contained diethyl ether and 3,3,3-trifluoro-2-(trifluoromethyl) lactic acid [12]. The amount of ether can be determined after water has been bound with phosphoric oxide and gases have been driven off. The 3,3,3-trifluoro-2-(trifluoromethyl) lactic acid was titrated with Bromophenol Blue as indicator, and the amount of perfluoroacetone was calculated from the difference in the titrations to phenolphthalein and to Bromophenol Blue. In various experiments, 100 ml of the "hydrate" contained from 67 to 83 g of perfluoroacetone.

A three-necked flask fitted with stirrer, thermometer, and reflux condenser was charged with 300 ml of concentrated sulfuric acid and was cooled externally with ice water while 100 ml of "perfluoroacetone hydrate" (b.p. 90-126; containing 67.5 g of perfluoroacetone according to titration data) was added. When the vigorous reaction was complete, the solution was heated slowly until gas ceased to be liberated (110-120° in the liquid). The gas liberated was purified with sulfuric acid and anhydrous potassium fluoride, dried over phosphoric oxide, and condensed in a trap cooled in solid carbon dioxide. This gave 65.6 g (98%) of anhydrous perfluoroacetone, which was used immediately in the following experiment.

β,β-Bistrifluoromethyl-β-propiolactone (I)

Preparation from Perfluoroacetone and Ketene. A four-necked flask fitted with stirrer, reflux condenser, and two gas-inlet tubes which passed to the bottom of the flask was charged with 50 ml of ether and was cooled to -78° while, over a period of two hours, 123 g (0.74 mole) of perfluoroacetone and 40 g (1 mole) of ketene were passed in simultaneously and condensed. The flask was then warmed slowly up to room temperature, and 10 g of phosphoric oxide was added to the solution. On the next day the solution was decanted from the precipitate and fractionated through a column having a 400-mm filling. We obtained 129.6 g (96%) of the lactone (I); b.p. 94.5-95° (775 mm); n_D^{20} 1.3240; d_4^{20} 1.6561; found MR 26.75; calculated MR 26.04; λmax: 5.29μ; 5.13μ. Found: C 28.65; H 1.25; F 52.02%. $C_5H_2F_6O_2$. Calculated: C 28.8; H 0.94; F 54.8%.

Preparation from 4,4,4-Trifluoro-3-hydroxy-3-(trifluoromethyl) butyric Acid. A mixture of 15.69 g (0.0678 mole) of the hydroxy acid (III) and 15 g (0.118 mole) of phosphoric oxide was heated in a metal bath to 150°; at this temperature a colorless liquid, b.p. 95-106°, slowly distilled off. Redistillation through a column gave 10.5 g (73%) of the lactone (I), b.p. 94.8-95° (745.6 mm) and n_D^{20} 1.3240.

3,3,3-Trifluoro-2-(trifluoromethyl) propene (II)

The pyrolysis of the lactone (I) was carried out in an apparatus consisting of a scaled-down copy of a ketene lamp [13]. The lactone (11.72 g) was subjected to pyrolysis on a nichrome spiral at 340-352°. The temperature was measured with a thermocouple, the hot junction of which was soldered to the middle of the spiral. The gases, after passing through a wash bottle containing water and a calcium chloride column, were condensed in two traps cooled by a mixture of solid carbon dioxide and acetone. The uncondensed gas was collected in a gas holder. We obtained 1.1 liters of carbon dioxide and 5.9 g (68%) of (II) (on the amount of lactone that reacted); b.p. 13.0-13.1° Found: C 29.35; H 1.25; F 68.94%; M 162. $C_4F_6H_2$. Calculated: C 29.30; H 1.22; F 69.5%; M 164. The literature [14] gives b.p. 11-13°.

Distillation of the residue gave 0.8 g of the lactone (I), b.p. 94-100°, and 1.6 g (15%) of an acid of b.p. 152-158° and identical to (XI).

4,4,4-Trifluoro-3-hydroxy-3-(trifluoromethyl) butyric Acid (III)

A mixture of 1.87 g (0.009 mole) of the lactone (I) and 0.3 g (0.016 mole) of water was heated for six hours in a sealed glass tube. After the product had been dried we obtained 2.02 g (99%) of the hydroxy acid

(III), m.p. 89-89.5° (from carbon tetrachloride); λmax 5.81μ. Found: C 26.35; H 1.73; F 50.31%. $C_5H_4F_6O_3$. Calculated: C 26.55; H 1.77; F 50.50%.

The lactone (I) (1.31 g) was mixed with 12 ml of concentrated sulfuric acid. When the exothermic reaction was complete, from the solution we distilled 1.36 g (96%) of crystals of m.p. 87-88° (from carbon tetrachloride), identical with (III). When concentrated hydrochloric acid was used instead of sulfuric acid, a short heating at 100° was required.

Dropwise addition of 35 ml of 2N NaOH was made to 10.16 g (0.049 mole) of the lactone (I). When the exothermic reaction was complete, the clear solution was decanted from the polymer formed and acidified. Extraction with ether gave 9.34 g (85%) of the hydroxy acid (III), m.p. 83-85°. After being washed with water and dried the polymer amounted to 1.34 g (13%).

The ester (V) (5.37 g) was boiled for one hour in 5 ml of anhydrous sulfuric acid, and from the reaction mixture we then distilled 4.58 g (96%) of (III), m.p. 87-88° (from carbon tetrachloride).

4,4,4-Trifluoro-3-hydroxy-3-(trifluormethyl) butyryl Bromide (IV)

A mixture of 10.58 g (0.051 mole) of the lactone (I) and 5.25 g (0.65 mole) of anhydrous hydrogen bromide was heated for eight hours at 100° in a sealed quartz tube. Excess of hydrogen bromide was evaporated off, and fractional distillation of the residue gave 6 g (41%) of pure (IV); b.p. 43.5-43.8° (21 mm); d_4^{20} 1.860; n_D^{20} 1.3775; found MR 35.79; $C_5H_3F_6O_2Br$. Calculated MR 35.43; Found: C 20.64; H 1.00; F 37.59%. $C_5H_3F_6O_2Br$. Calculated: C 20.8; H 1.04; F 39.4%.

When (IV) (0.3 g) was left in air, it was quantitatively converted into the hydroxy acid (III), m.p. 87-88.5° (from carbon tetrachloride). During slow distillation through a column at atmospheric pressure, (IV) is decomposed with liberation of hydrogen bromide and formation of the lactone (I), b.p. 92-95° and n_D^{20} 1.3233, 0.45 g (0.0015 M) (IV). At a temperature of -78°, (IV) (0.45 g, 0.0015 mole) was mixed with piperidine (0.5 g, 0.0028 mole). When the vigorous reaction was complete, piperidine was washed out with dilute hydrochloric acid and the product was dried. It amounted to 0.32 g (70%) of crystals, m.p. 60-61.5° (from heptane) and identical with (X).

Ethyl 4,4,4-Trifluoro-3-hydroxy-3-(trifluoromethyl) butyrate (V)

A mixture of 10.7 g (0.051 mole) of the lactone (I) and 15 ml of absolute alcohol was boiled for six hours and then poured into water. Extraction with ether gave 10.000 g (77%) of the ester (V), b.p. 157-158° (756 mm) and n_D^{20} 1.3432, identical with the compound described in [10].

Analogous experiments, in which concentrated sulfuric acid or sodium ethoxide was used as catalyst, gave the ester (V) in 77% or 74% yield, respectively. On esterification of 10.0 g of the hydroxy acid (III) with 40 ml of absolute ethanol in presence of 1 ml of concentrated sulfuric acid we obtained 6.35 g (61%) of the ester (V), b.p. 154-156° (746.3 mm) and n_D^{20} 1.3432. In none of the experiments was the ethoxy acid isolated.

4,4,4-Trifluoro-3-hydroxy-3-(trifluoromethyl) butyramide (VI)

A mixture of 0.56 g of the ester (V) and 4.5 ml of concentrated aqueous ammonia was shaken until the whole of the ester dissolved. After evaporation of ammonia and drying, 0.31 g (63%) of the amide (VI), m.p. 83.5-84.5° (from dry benzene), was obtained. Found: C 27.25; H 2.44; F 51.55, N 6.23%. $C_5H_5F_6O_2N$. Calculated: C 26.65; H 2.46; F 50.06; N 6.23%.

The lactone (I) (0.99 g) was mixed with 10 ml of concentrated aqueous ammonia. When the exothermic reaction was complete we obtained 1.05 g (98%) of crystals of m.p. 84-84.5° (from benzene), identical with (VI).

4,4,4-Trifluoro-3-hydroxy-N,N-dimethyl-3-(trifluoromethyl) butyramide (VII)

Dry dimethylamine (6.1 g, 0.13 mole) was passed for one hour into a solution of 8.9 g (0.042 mole) of the lactone (I) in 15 ml of acetonitrile cooled to 0°. After evaporation of the excess of dimethylamine and acetonitrile we obtained 8.59 g of the amide (VII), m.p. 63-63.5° (from heptane). Found: C 33.26; H 3.67; F 44.44; N 5.70%. $C_7H_8F_6O_2N$. Calculated: C 33.3; H 3.18; F 45.3; N 5.56%.

Aqueous dimethylamine and the lactone (I) gave (VII) in quantitative yield. All the amides [(VII)–(X)] obtained are soluble in 10% potassium hydroxide solution and insoluble in dilute acids.

N-Ethyl-4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyramide (VIII)

By reaction of ethylamine with the lactone (I) at -78° we obtained the amide (VIII) in 84% yield; m.p. 47-47.5° (from carbon tetrachloride). Found: C 32.93; H 3.58; F 44.44; N 5.77%. $C_7H_8F_6O_2N$. Calculated: C 33.3; H 3.18; F 45.3; N 5.56%.

4,4,4-Trifluoro-3-hydroxy-3-(trifluoromethyl) butyranilide (IX)

From 1.02 g (0.005 mole) of the lactone (I) and 0.5 g (0.0052 mole) of aniline we obtained 1.31 g (89%) of the amide (IX), m.p. 100-100.5° (from carbon tetrachloride). Found: C 43.75; H 2.89; F 36.03; N 5.14%. $C_{11}H_8F_6O_2N$. Calculated: C 44.0; H 2.66; F 38.0; N 4.67%.

Piperidide of 4,4,4-Trifluoro-3-hydroxy-3-(trifluoromethyl) butyric Acid

This was prepared from the lactone (I) and piperidine in 92% yield; m.p. 62-62.5° (from carbon tetrachloride). Found: C 40.97; H 4.40; F 39.72; N 4.78%. $C_{10}H_{13}F_6O_2N$. Calculated: C 41.0; H 4.44; F 38.95; N 4.78%.

4,4,4-Trifluoro-3-(trifluoromethyl) crotonic Acid

From β,β-Bistrifluoromethyl-β-propiolactone. The lactone (I) (3.12 g) was mixed with 2 ml of anhydrous sulfuric acid. When the exothermic reaction was complete, 2.92 g (94%) of colorless liquid, b.p. 157-163°, was distilled off; redistillation of this gave pure (XI); b.p. 158-158.5° (762.1 mm); m.p. 28.5-29.5°; neutralization equivalent 205; calculated 208; λ_{max} 5.71μ. Found: C 28.85; H 0.94; F 52.89%; $C_5H_2F_6O_2$. Calculated: C 28.8; H 0.96; F 54.9%. The acid formed white needles which deliquesced in air; it formed a 58% solution with water. When the ether complex of boron trifluoride was used instead of sulfuric acid, boiling for several hours was necessary and the yield of the acid (XI) was then 82%.

From 4,4,4-Trifluoro-3-hydroxy-3-(trifluoromethyl) butyric Acid. A mixture of 1.65 g of the hydroxy acid (III) and 2 ml of anhydrous sulfuric acid was heated for 15 minutes at 100°, and distillation then gave 1.39 g (91%) of crystals of m.p. 28-29.5° (from heptane), identical with (XI).

Polymerization of β,β-Bistrifluoromethyl-β-propiolactone

Addition of 0.01 g of sodium or traces of triethylamine to 13.32 g of the lactone (I) and keeping of the mixture at 20° for four days led to the formation of a thick colorless polymer which softened at 30-40°. Its molecular weight, determined cryoscopically, was 1310. The polymer (1.32 g) and anhydrous sulfuric acid (2 ml) were heated together until complete solution occurred (ten minutes), and from the mixture 1.14 g of the acid (XI), b.p. 157-159° (742 mm) and m.p. 26-29°, was then distilled off. The polymer (1.31 g) was dissolved in 10 ml of 10% potassium hydroxide solution. Acidification and extraction with ether gave 0.96 g (73%) of the hydroxy acid (III), m.p. 87-89° (from carbon tetrachloride). The polymer (8.2 g) was treated in ethereal solution with dilute hydrochloric acid. The solution was dried, solvent was distilled off, and pyrolysis of the residue at 160-180° gave 5.84 g of the acid (XI).

SUMMARY

1. The reaction of perfluoroacetone with ketene was carried out and led to the formation of β,β-bistrifluoromethyl-β-propiolactone [4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid β-lactone].

2. It was shown that the β-hydroxy acid, i.e., 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid or its acid bromide, can be cyclized into the β-lactone.

3. The opening of the four-membered ring of β-β-bistrifluoromethyl-β-propiolactone, unlike that of β-isovalerolactone, proceeds exclusively in one direction with formation of derivatives of 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid.

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FLUORINATED KETONES

COMMUNICATION 1. PERFLUOROACETONE AND ITS REACTIONS WITH ALCOHOLS, ORGANOMETALLIC COMPOUNDS, AND COMPOUNDS CONTAINING MOBILE HYDROGEN

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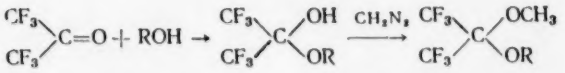
Fluorinated ketones have recently attracted the attention of various investigators [1]. However, the chemical properties of the most accessible perfluoro ketone, perfluoroacetone, have as yet received scarcely any study. It is known only that it forms a stable hydrate, a semicarbazone [2], and a 2,4-dinitrophenylhydrazone and that it is decomposed by alkalis into fluoroform and a trifluoroacetate [4]. The more detailed study of the properties of perfluoroacetone formed the subject of the present work.

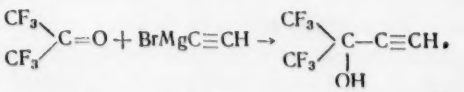
Perfluoroacetone reacts vigorously with alcohols with formation of unstable hemiketals, which are difficult to purify and which decompose, when heated, into the original reactants. However, treatment of the hemiketals with diazomethane leads to the formation of quite stable symmetric and unsymmetric ketals:



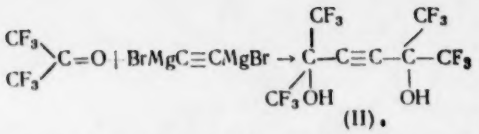
in which R = CH_3, C_2H_5, $CH_2C_6H_5$.

Perfluoroacetone ketals are slowly hydrolyzed by concentrated alkalis, but remain unchanged during prolonged boiling with aniline and when kept at room temperature in contact with dilute acids. Whereas acetone ketals are completely hydrolyzed when shaken with dilute acids in the cold, perfluoroacetone dimethyl ketal is not completely hydrolyzed even after boiling for five hours with 2N HCl.

Reaction of perfluoroacetone with organomagnesium compounds gives tertiary alcohols, which form azeotropes with ether; these azeotropes can be broken down only by treatment with concentrated sulfuric acid. The formation of azeotropes can be avoided by carrying out the reaction in dibutyl ether. Unlike trifluoroacetone, whose condensation with ethynylmagnesium bromide gives the diol together with very small amounts of 2-(trifluoromethyl)-3-butyn-2-ol [5], perfluoroacetone gives 1,1,1-trifluoro-2-(triflouromethyl)-3butyn-2-ol (I) in 58% yield in the same reaction. However, on condensation with ethynylenebis [magnesium bromide] it gives mainly the diol (II):

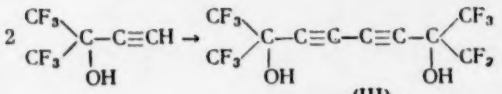


(I)



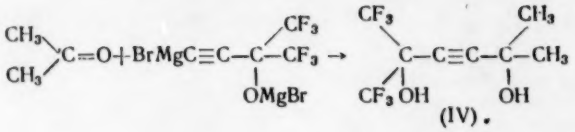
(II).

Oxidation of (I) with oxygen in presence of cuprous chloride gave hexafluoro-2,7-bistrifluoromethyl-3,5-octadiyne-2,7-diol (III):



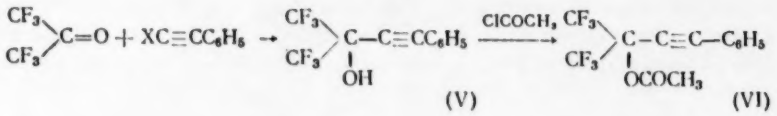
(III).

Reaction of acetone with the magnesium derivative of 1,1,1-trifluoro-2-(trifluoromethyl)-3-butyn-2-ol gave the unsymmetric diol (IV):



(IV).

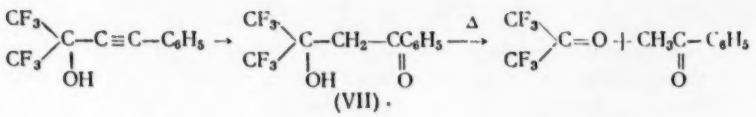
Reaction occurred readily also with (phenylethynyl) magnesium bromide with formation of 1,1,1-trifluoro-4-phenyl-2-(trifluoromethyl)-3-butyn-2-ol (V) in 84% yield. In somewhat poorer yield, (V) was formed also in the condensation of perfluoroacetone with (phenylethynyl) sodium. Acetylation of the alcohol gave the corresponding acetic ester (VI):



(V) (VI)

in which X = Na, MgBr.

Unlike nonfluorinated α-acetylenic alcohols, which are either dehydrated or rearranged into α,β-unsaturated ketones under the action of acids, (V) remained unchanged when heated with 68% sulfuric acid. However, when treated with concentrated sulfuric acid or warmed with 60% sulfuric acid in presence of mercuric acetate, it gave the hydration product, 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyrophenone (VII), in 82% yield:

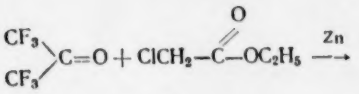


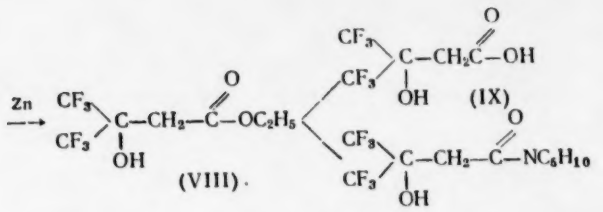
(VII).

The presence of a hydroxy group in (VII) was proved by the formation of metal derivatives under the action of alkalis, and the carbonyl group was detected by infrared spectroscopy.

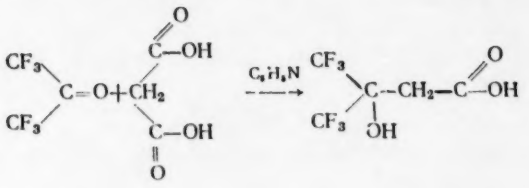
With prolonged heating at 250-300°, 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyrophenone decomposed into perfluoroacetone and acetophenone with cleavage of a C–C bond. (VII) behaved similarly when heated with an excess of phosphoric oxide. Decomposition of this sort is unusual for β-hydroxy ketones, which are generally converted by heat into α, β-unsaturated ketones; it indicates the immobility of a hydroxy group attached to a carbon carrying two trifluoromethyl groups. The same inertness of a hydroxy group is shown also

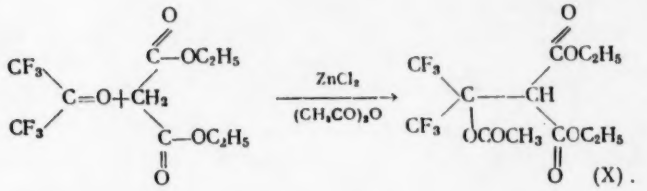
in ethyl 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyrate (VIII), which is obtained from perfluoroacetone by the Reformatskii reaction. (VIII) is hydrolyzed by alkalis into 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid (IX), and with piperidine it gives the piperidide of the acid; but attempts to convert it into 4,4,4-trifluoro-3-(trifluoromethyl) crotonic acid by heating it with phosphoric oxide to 250° were not successful:



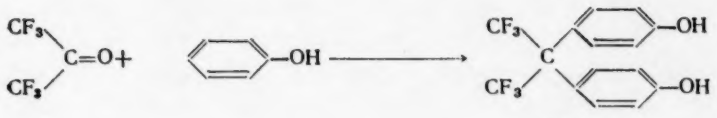


Perfluoroacetone reacts extremely readily, with evolution of much heat, with malonic acid in presence of pyridine. The reaction, which is analogous to that with trifluoroacetone [5], gives an almost quantitative yield of 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid. In presence of acetic anhydride and anhydrous zinc chloride, malonic ester gives diethyl [1-acetoxy-2,2,2-trifluoro-1-(trifluoromethyl) ethyl] malonate (X):



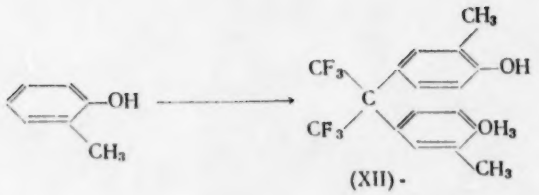


Perfluoroacetone reacts also with aromatic compounds containing mobile hydrogens in the ring. Thus, when perfluoroacetone is heated with phenol or o-cresol* in anhydrous hydrogen fluoride as solvent, an almost quantitative yield is obtained of 4,4'-(hexafluoroisopropylidene) diphenol (XI) or 4,4'-(hexafluoroisopropylidene) di-o-cresol (XII):



(XI)

* Under these conditions p-cresol does not react with perfluoroacetone.



(XII).

These compounds are very interesting as possible monomers in the preparation of polyesters, polyurethans, etc.

EXPERIMENTAL

General Method for the Preparation of Perfluoroacetone Hemiketals and Ketals. Perfluoroacetone was passed into an equimolecular amount of a cooled alcohol. The reaction was strongly exothermic. The reaction mixture was fractionated. The following hemiketals were obtained:

Perfluoroacetone methyl hemiketal (50%); b.p. 48-51° (130 mm); n_D^{20} 1.3095; d_4^{20} 1.4606. Found: C 25.81; H 2.98%. $C_4H_4F_6O_2$. Calculated: C 24.25; H 2.03%.

Perfluoroacetone ethyl hemiketal (41%); b.p. 51.52° (80 mm); n_D^{20} 1.330; d_4^{20} 1.2634. Found: C 31.96; H 4.59; F 44.09%. $C_5H_6F_6O_2 \cdot C_2H_5OH$. Calculated: C 32.56; H 4.61; F 44.14%.

Perfluoroacetone benzyl hemiketal (65%); b.p. 81-82° (14mm); n_D^{20} 1.4690; d_4^{20} 1.2650. Found: C 44.30; H 3.23%. $C_{10}H_8F_6O_2$. Calculated: C 43.81; H 3.32%.

Perfluoroacetone hemiketals are colorless liquids which are soluble in water; when heated, they dissociate into the original reactants. By treatment of ethereal solutions of the hemiketals with diazomethane, the following ketals were obtained:

Perfluoroacetone dimethyl ketal (60%); b.p. 85.5-83.5°; n_D^{20} 1.3050; d_4^{20} 1.3981; found MR 28.84; calculated MR 29.42; Found: C 28.19; H 2.98; F 53.13%. $C_5H_6F_6O_2$. Calculated: 28.30; H 2.83; F 53.77%.

Perfluoroacetone ethyl methyl ketal; b.p. 95-96°, n_D^{20} 1.3172; d_4^{20} 1.3345; found MR 33.33; calculated MR 34.04. Found: C 31.42; H 3.55; F 50.44%. $C_6H_8F_6O_2$. Calculated: C 31.86; H 3.54; F 50.44%.

General Method for the Preparation of Alkyl (or Aryl) bistrifluoromethylmethanols. Under ice-salt cooling, perfluoroacetone was passed into a vigorously stirred equimolecular amount of Grignard reagent dissolved in diethyl or dibutyl ether. On the next day the reaction mixture was hydrolyzed with dilute acid, and the ether extracts were fractionally distilled*.

The following alcohols were obtained:

Methylbistrifluoromethylmethanol (62%); b.p. 60.5-61.5° (azeotrope with ether, b.p. 71-72°); n_D^{20} 1.3030; d_4^{20} 1.4840; found MR 23.13; calculated MR 23.03. Found: C 27.09; H 2.23; F 61.83%. $C_4H_4F_6O$. Calculated: C 26.37; H 2.19; F 62.63%.

With phenyl isocyanate in presence of pyridine this alcohol forms a phenylurethan, m.p. 96.5-97.5° (from petroleum ether). Found: C 43.70; H 3.02; F 37.75%. $C_{11}H_9F_6NO_2$. Calculated: C 43.85; H 2.99; F 37.87%.

Ethylbistrifluoromethylmethanol (47%); b.p. 73-74° (azeotrope with ether, b.p. 81-82°); n_D^{20} 1.3245; d_4^{20} 1.4358; found MR 27.38; calculated MR 27.60. Found: C 29.73; H 3.06; F 58.29%. $C_5H_6F_6O$. Calculated: C 30.61; H 3.06; F 58.16%.

* When the reaction was carried out in diethyl ether, the reaction product was washed with concentrated sulfuric acid before fractionation.

Phenylbistrifluoromethylmethanol (60%); b.p. 72-73° (35 mm); n_D^{20} 1.4145; d_4^{20} 1.4510; found MR 42.06; calculated MR 42.52. Found: C 43.55; H 2.59; F 46.71%. $C_9H_6F_6O$. Calculated: C 44.27; H 2.47; F 46.72%.

1,1,1-Trifluoro-2-(trifluoromethyl)-3-butyn-2-ol (I). A round-bottomed flask fitted with stirrer, tube for passage of gas, dropping funnel, and condenser cooled with solid carbon dioxide was charged with 100 ml of tetrahydrofuran, which was then saturated with acetylene; gradual addition was made of a Grignard reagent obtained from 4.3 g of magnesium and 19.2 g of ethyl bromide in 80 ml of tetrahydrofuran; passage of acetylene was continued throughout. There was a precipitate of ethynylmagnesium bromide. The mixture was stirred vigorously and cooled with ice and salt while 21.7 g of perfluoroacetone was passed in. On the next day the reaction mixture was hydrolyzed with dilute hydrochloric acid, and by fractionation of the tetrahydrofuran solution we isolated the azeotropic mixture of (I) with tetrahydrofuran, b.p. 61-62° (80 mm), from which, by treatment with concentrated sulfuric acid, we isolated 14.6 g (57.9%) of (I); b.p. 77.5-78.5°; n_D^{20} 1.3205; d_4^{20} 1.4664; found MR 26.05; calculated MR 25.61. Found: C 30.77; H 1.31; F 59.25%. $C_5H_2F_6O$. Calculated: C 31.25; H 1.04; F 59.37%.

Hexafluoro-2,5-bistrifluoromethyl-3-hexyne-2,5-diol (II). By similar reaction, but with 100% excess of ethylmagnesium bromide, we obtained 4.4 g (17.3%) of 1,1,1-trifluoro-2-(trifluoromethyl)-3-butyn-2-ol and 15.3 g of the azeotrope formed by (II) with tetrahydrofuran, b.p. 66-67° (8 mm); from this by treatment with concentrated sulfuric acid we isolated 9 g (40%) of (II), m.p. 59-60° (from carbon tetrachloride). Found: C 26.77; H 0.56%; $C_8H_2F_{12}O_2$. Calculated: C 26.81; H 0.58%.

Hexafluoro-2,7-bistrifluoromethyl-3,5-octadiyne-2,7-diol (III). Oxygen was passed for several hours through a mixture of 2 g of cuprous chloride, 6 g of ammonium chloride, and 4.7 g of 1,1,1-trifluoro-2-(trifluoromethyl)-3-butyn-2-ol. After several days, 20 ml of 20% hydrochloric acid was added to the reaction mixture; a precipitate formed, and was filtered off and washed with water. This gave 4 g (83.3%) of (III). m.p. 70-71° (from carbon tetrachloride). Found: C 29.93; H 1.01; F 56.52%. $C_{10}H_2F_{12}O_2 \cdot H_2O$ Calculated: C 30.00; H 1.00; F 57.00%.

Water of crystallization was removed by a ten-hour treatment at 50-55° over phosphoric oxide. Found: C 30.95; H 0.54; F 59.10%. $C_{10}H_2F_{12}O_2$. Calculated: C 31.41; H 0.52; F 59.68%.

1,1,1-Trifluoro-5-methyl-2-(trifluoromethyl)-3-hexyne-2,5-diol (IV). 1,1,1-Trifluoro-2-(trifluoromethyl)-3-butyn-2-ol (4.9 g) was added to a Grignard reagent prepared from 1.22 g of magnesium and 5.5 g of ethyl bromide. After one hour 1.5 g of acetone was added. After hydrolysis and removal of ether we obtained 2.3 g (63%) of (IV), m.p. 77-78° (from dichloroethane). Found: C 38.62; H 3.15; F 45.53%. $C_8H_8F_6O_2$. Calculated: C 38.40; H 3.2; F 45.6%.

1,1,1-Trifluoro-4-phenyl-2-(trifluoromethyl)-3-butyn-2-ol (V). With ice-salt cooling and stirring, 35.7 g of perfluoroacetone was passed into a suspension of 9.3 g of (phenylethynyl) sodium in dry ether. After hydrolysis and fractionation of the reaction mixture we obtained 42.4 g (76% of (V); b.p. 81-82° (7 mm); n_D^{20} 1.4470; d_4^{20} 1.3745. Found: C 48.75; H 2.01; F 43.60. $C_{22}H_6F_6O$. Calculated: C 49.25; H 2.20; F 42.54.

Reaction under the same conditions, but with (phenylethynyl) magnesium bromide, gave (V) in 84% yield.

1,1,1-Trifluoro-4-phenyl-2-(trifluoromethyl)-3-butyn-2-ol Acetic Ester (VI). Sodium wire (1.44 g) was added to a solution of 16.9 g of (V) in ether, and then, after the dissolution of the sodium, 8 g of acetyl chloride was added. Fractionation gave 15.5 g (81%) of (VI); b.p. 81-82° (3 mm); n_D^{20} 1.4440; d_4^{20} 1.3297. Found C 50.35; H 2.63; F 36.50%. $C_{31}H_8F_6O_2$. Calculated: C 50.32; H 2.58; F 36.77%.

4,4,4-Trifluoro-3-hydroxy-3-(trifluoromethyl) butyrophenone (VII). A stirred mixture of 17.7 g of (V), 40 ml of 60% sulfuric acid, and 0.95 g. of mercuricacetate was heated for 15 hours in a boiling water bath. The reaction mixture was diluted with water and extracted with ether. Solvent was distilled off and we obtained 15.4 g (82%) of (VII); b.p. 81.5-82.5° (2 mm); n_D^{20} 1.4460; d_4^{20} 1.4720; found MR 53.22; calculated MR 51.66; λ_{max} 5.99; 6.25 μ. Found: C 46.47; H 2.74; F 39.59%. $C_{11}H_8F_6O_2$. Calculated: C 46.15; H 2.79; F 39.89%.

(VII) was formed also (55% yield) by keeping (V) in contact with concentrated sulfuric acid for two days.

(VII) (4.27 g) was heated for eight hours in a metal bath at 270-300°. The semicarbazone obtained from the perfluoroacetone liberated during the reaction had m.p. 154°, undepressed by admixture of known perfluoroacetone semicarbazone. From the liquid remaining after the decomposition of (VII) we obtained 3.2 g (65%) of acetophenone dinitrophenylhydrazone m.p. 236-238°, undepressed by admixture of a known sample.

Ethyl 4,4,4-Trifluoro-3-hydroxy-3-(trifluoromethyl) butyrate (VIII). A round-bottomed flask fitted with stirrer, tube for the passage of gas, dropping funnel, and condenser cooled with solid carbon dioxide was charged with a mixture of 7.1 g of zinc dust, 50 ml of benzene, and 50 ml of dry ether. External cooling with ice and salt was applied, the mixture was stirred, 16.2 g of perfluoroacetone was passed, and 16.2 g of ethyl bromoacetate was gradually dropped in; finally, the mixture was heated for one hour in a water bath. Hydrolysis and fractionation of the reaction mixture gave 10.2 g (41%) of (VIII); b.p. 73.5-74.5° (40 mm); n_D^{20} 1.3438; d_4^{20} 1.4106; found MR 38.14; calculated MR 38.35. Found: C 33.10; H 3.10; F 45.66%. $C_7H_8F_6O_3$. Calculated: C 33.07; H 3.15; F 44.88%.

A mixture of 1 g of (VIII) and 2.5 ml of 10% NaOH solution was heated for two hours in a water bath. Acidification and extraction with ether gave 0.5 g (62%) of crystals of m.p. 88-89°, identical with 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid (IX) [6].

A mixture of 1.35 g of (VIII) and 2.2 g of piperidine was heated for eight hours in a water bath. The mixture was acidified with hydrochloric acid. This gave 1.32 g (94%) of crystals of m.p. 61-62° (from aqueous alcohol), identical with the piperidide of 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid obtained from β,β,-bistrifluoromethyl-β-propiolactone [6].

4,4,4-Trifluoro-3-hydroxy-3-(trifluoromethyl) butyric Acid (IX). Perfluoroacetone (8 g) was passed into a solution of 6 g of malonic acid in 10 g of piperidine. On the next day the reaction mixture was dissolved in water, and the solution was acidified with hydrochloric acid and extracted with ether. Ether was distilled off, and there remained 10.5 g (96%) of crystals of m.p. 88-89° (from benzene), identical with the 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyric acid (IX) obtained by the hydrolysis of β,β-bistrifluoromethyl-β-propiolactone [6].

Diethyl [1-acetoxy-2,2,2-trifluoro-1-(trifluoromethyl) ethyl] malonate (X). A mixture of 10 g of acetic anhydride, 3.5 g of zinc chloride, and 12 g of perfluoroacetone was heated in a sealed tube for ten hours at 100°. After decomposition of the acetic anhydride with water we obtained 9.6 g (41.7%) of (X); b.p. 112-113° (10 mm); n_D^{20} 1.3842; d_4^{20} 1.3608; found MR 63.12; calculated MR 63.11. Found: C 39.33; H 3.88; F 31.08%. $C_{12}H_{14}F_6O_6$. Calculated: C 39.08; H 3.80; F 30.97%.

4,4'-(Hexafluoroisopropylidene) diphenol (XI). Perfluoroacetone (16 g) was added to a mixture of 17.8 g of phenol and 32 g of anhydrous hydrogen fluoride cooled with solid carbon dioxide. The mixture was heated in a sealed tube for ten hours in a boiling water bath and was then poured into a copper vessel. When hydrogen fluoride had evaporated, unchanged phenol was steam-distilled off. Crystallization of the residue from dichloroethane gave 29 g (90.5%) of (XI), m.p. 161-162°. Found: C 53.68; H 2.98; F 34.13%. $C_{15}H_{10}F_6O_2$. Calculated: C 53.57; H 2.97; F 33.92%.

4,4'-(Hexafluoroisopropylidene) di-o-cresol (XII). The procedure was analogous to that of the preceding experiment. From 7.1 g of o-cresol, 15 g of anhydrous hydrogen fluoride, and 5.5 g of perfluoroacetone we obtained 10.9 (91%) of (XII), m.p. 134-135° (from carbon tetrachloride). Found: C 55.98; H 3.84; F 31.76%. $C_{17}H_{14}F_6O_2$. Calculated: C 56.31; H 3.84; F 31.32%.

SUMMARY

1. A study was made of the reactions of perfluoroacetone with alcohols, organometallic compounds, and compounds containing mobile hydrogen.

2. Hemiketals, ketals, tertiary alcohols, symmetric and unsymmetric diols, and β-hydroxy acids containing two trifluoromethyl groups were synthesized.

3. 4,4,4-trifluoro-3-hydroxy-3-(trifluoromethyl) butyrophenone, obtained by the hydration of 1,1,1-trifluoro-4-phenyl-2-(trifluoromethyl-3-butyn-2-ol, decomposes when heated into perfluoroacetone and acetophenone with cleavage of a C—C bond. Decomposition in this way, which is unusual for β-hydroxy ketones, indicates the immobility of a hydroxy group attached to a carbon carrying two trifluoromethyl groups.

4. When perfluoroacetone is heated with phenol or o-cresol in anhydrous hydrogen fluoride solution, 4,4'-(hexafluoroisopropylidene) diphenol or 4,4'-(hexafluoroisopropylidene) di-o-cresol, respectively, is formed.

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* Original Russian pagination. See C.B. translation.

EFFECT OF α-HYDROXY AND α-ACETOXY GROUPS ON THE CHARACTER OF THE REACTION OF HYPOBROMOUS ACID WITH CARBON – CARBON MULTIPLE BONDS

COMMUNICATION 1. CASES OF AN ANOMALOUS COURSE IN THE FAVORSKII REACTION

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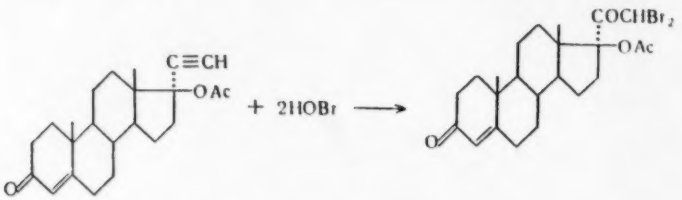
The addition of hypochlorous acid to a triple carbon-carbon bond [1] was discovered and studied in detail by Favorskii in 1894. He then showed that in the reaction of hypochlorous acid with acetylenic compounds the corresponding α,α-dichloro ketones are formed in good yield. In 1900 this reaction was extended to hypobromous acid [1].

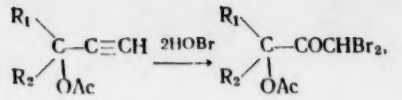
$$R\cdot C\equiv CH \xrightarrow{2HOX} RCOCHX_2 + H_2O$$

in which X = Cl, Br.

Favorskii regarded this reaction as the addition of the elements of hypobromous acid (two molecules) to a triple bond with simultaneous elimination of one molecule of water. He did not make a closer study of the mechanism. In 1947 Reichstein and Salomon [2] applied Favorskii's reaction to acetylenic alcohols of the steroid series and to their acetates. They showed that in the case of the acetates of acetylenic alcohols [2] normal addition of hypobromous acid to a triple carbon-carbon bond occurs with formation of the acetates of the corresponding α,α-dibromo ketones in high yield.

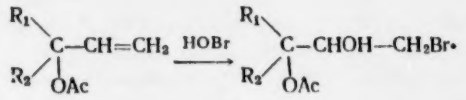


When acetylenic alcohols were used in the reaction they isolated bromine-containing products of unestablished structure. In an investigation of various ways of introducing oxidized side chains characteristic for corticosteroids into cyclic compounds, in 1952 Nazarov and the present author examined the Favorskii reaction and applied it to aliphatic and alicyclic acetylenic alcohols and their acetates. We then showed [3] that hypobromous acid reacts normally with the triple bond of α-acetates of aliphatic and alicyclic tertiary acetylenic alcohols with formation of the acetates of the corresponding dibromo ketols [4].

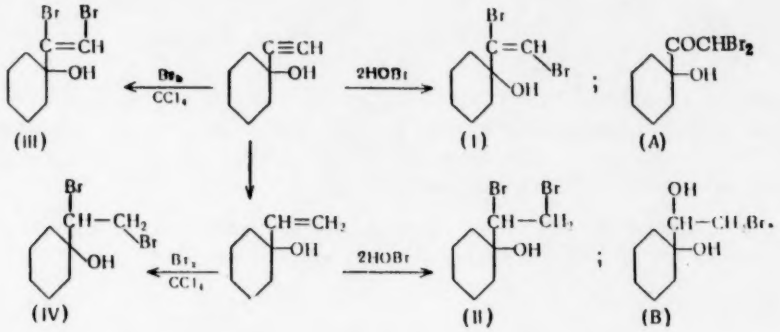


in which $R_1 = R_2 = CH_3$, $-CH_2-(CH_2)_3-CH_2-$ and others.

The acetates of tertiary ethylenic alcohols also give normal reaction products with hypobromous acid, i.e., acetates of ω-bromo diols:



Tertiary acetylenic and ethylenic alcohols behave differently in this reaction and, instead of the expected normal reaction products [dibromo ketols (A) and ω-bromo diols (B)], they give the dibromo compounds (I) and (II), apparently of trans- and erythro-configurations (ionic addition) [3].



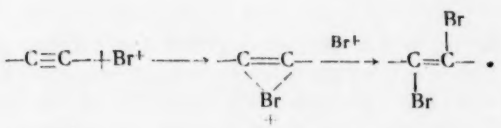
It was shown earlier [5] that, in the light, N-bromoacetamide can serve as a substitute for bromine and brominate a multiple bond (in nonionic solvents):

$$CH_3CONHBr + h\nu \longrightarrow CH_3CONH^{\cdot} + Br^{\cdot} \quad (1)$$

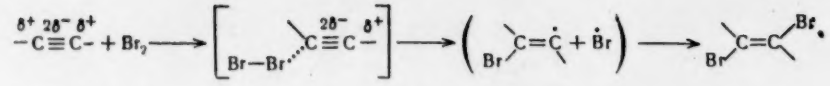
$$>C=C< + Br^{\cdot} \longrightarrow >CBr-\dot{C}< \quad (2)$$

$$>CBr-C< + CH_3CONHBr \longrightarrow >CBr-CBr< + CH_3CO\dot{N}H. \quad (3)$$

The dibromo compounds (III) and (IV), apparently of cis- and threo-configurations, are obtained by the bromination of acetylenic and ethylenic alcohols with bromine in carbon tetrachloride. Until recently it was assumed that bromination under ionic conditions proceeds through the intermediate formation of a complex of the bromine ion with the multiple bond of the π-complex type [6] and always leads to the formation of trans-addition products:

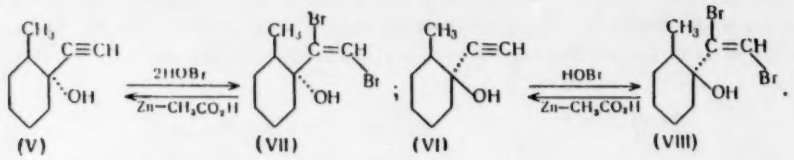


It was recently [7] shown that the formation of a bromonium π-complex is impossible in the case of an acetylenic triple bond. In the opinion of the author [7] bromination proceeds in this case in accordance with the scheme:



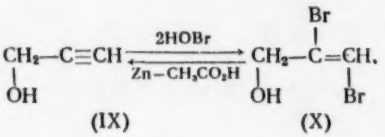
Here, trans addition is explained by the formation of an intermediate trans radical, to which a bromine radical then adds with formation of a trans dibromo compound.

In order to follow the effect of neighboring hydroxy and acetoxy groups, and also of a chlorine atom, on the character of the reaction of hypobromous acid with multiple bonds, we extended the reaction to some acetylenic alcohols and diols containing tertiary and primary alcohol groups and to their acetates. It was found that in the case of cis- and trans-1-ethynyl-2-methylcyclohexanols (V) and (VI) [8] the reaction of hypobromous acid with the triple bond is again anomalous and gives the corresponding unsaturated dibromo alcohols (VII) and (VIII), which are apparently of trans-configuration (with respect to the double bond):

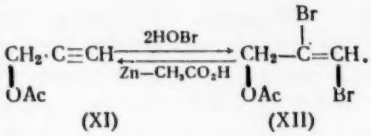


The dibromo compounds (VII) and (VIII) were converted into the original acetylenic alcohols (V) and (VI) by boiling them with zinc dust in acetic acid [2, 3], which proves their structure. Unlike the acetylenic alcohols (V) and (VI), their acetates, as we have shown previously [9], undergo normal addition of hypobromous acid at the triple bond with formation of the corresponding acetates of dibromo ketols.

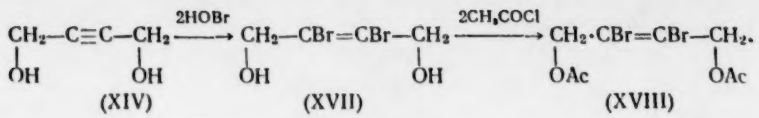
When hypobromous acid reacts with 2-propyn-1-ol (IX), interaction at the triple bond is anomalous with formation of an ethylenic dibromo alcohol (X) of trans-configuration:



The result obtained in the reaction of hypobromous acid with 2-propyn-1-ol acetate (XI), which contains a primary acetoxy group, was somewhat unexpected. In this case, as in the case of the alcohol (IX), there was anomalous reaction of hypobromous acid with the triple bond and, instead of the expected dibromo ketol acetate (XIII), the dibromo acetic ester (XII), apparently of trans-configuration, was obtained:

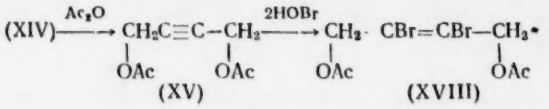


When the dibromo alcohol (X) and its acetate (XII) were treated with zinc dust in acetic acid, their debromination occurred with formation of the original 2-propyn-1-ol (IX) and its acetate (XI), which gave characteristic tests for acetylenic hydrogen with ammoniacal silver nitrate solution. A similar anomaly in the reaction of hypobromous acid with a triple bond is observed also in the cases of 2-butyne-1,4-diol (XIV), its diacetate (XV), and 1,4-dichloro-2-butyne (XVI). In all these cases the corresponding unsaturated dibromo compound is formed. Thus, in the reaction of hypobromous acid with 2-butyne-1,4-diol (XIV) a good yield is obtained of the known [10] 2,3-dibromo-2-butene-1,4-diol (XVII), m.p. 113.5-114°, of unestablished configuration:



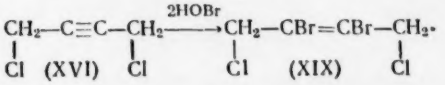
(XIV) (XVII) (XVIII)

When the butynediol (XIV) was brominated with bromine in the light in a medium of chloroform and carbon tetrachloride (conditions for nonionic addition) we did not succeed in isolating crystalline reaction products. Acetylation of the dibromo compound (XVII) with acetyl chloride gave a good yield of the diacetate (XVIII), m.p. 60-60.5°. The same diacetate (XVIII) is formed by the action of hypobromous acid on butynediol diacetate (XV):



(XV) (XVIII)

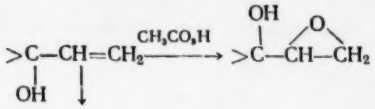
By reaction with hypobromous acid, 1,4-dichloro-2-butyne (XVI) gives the known [10] 2,3-dibromo-1,4-dichloro-2-butene (XIX), m.p. 59.5-60°, of unestablished configuration:

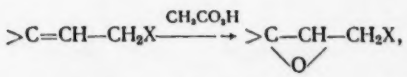


(XVI) (XIX)

The same dibromo dichloro compound (XIX) is formed in the bromination of the dichlorobutyne (XVI) with bromine in carbon tetrachloride in the light. Here there appears to be formed a mixture of cis- and trans-isomers, for in this experiment, together with crystals of the compound (XIX) of m.p. 59.5-60°, we obtained a partially crystallizing mother liquor which was not investigated more closely.

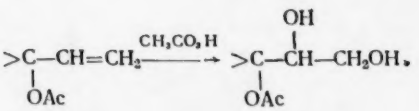
The effect of a neighboring tertiary acetoxy group on addition at a multiple bond was observed also for the case of the oxidation of a double bond with peroxyacetic acid. We have shown [3, 9] that tertiary ethylenic alcohols are oxidized normally with peroxyacetic acid with formation of the corresponding glycidols. Primary ethylenic alcohols and their acetates are oxidized in the same way.





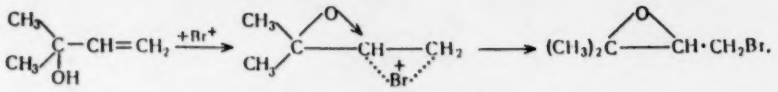
in which X=OH, OAc, Cl, Br.

However, acetates of tertiary ethylenic alcohols are oxidized with peroxy acids with much more difficulty than Prilezhaev stated [11], and the products are not acetates of glycidols, but acetates of triols [3, 9]:

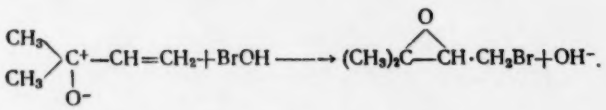


Winstein and Goodman, taking allyl alcohol and its acetate as examples [12], showed that neighboring primary hydroxy and acetoxy groups do not participate in the addition of electrophilic reagents to the multiple

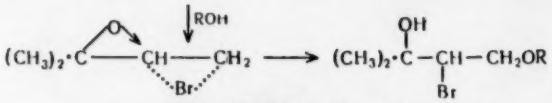
bond, whereas the neighboring tertiary hydroxy group in 2-methyl-3-buten-2-ol [13] takes part in the addition of the bromine cation to the double bond:



Under alkaline conditions, a hypobromite solution, even when free bromide ions are absent, converts 2-methyl-3-buten-2-ol almost completely into 1-bromo-2,3-epoxy-3-methylbutane:

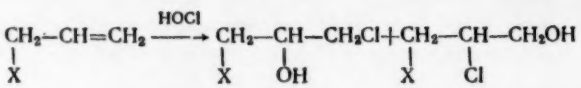


On this basis the reaction rate should be of first order and independent of the concentration of alkali, which was confirmed by kinetic measurements [13]. Solvent participates in the reaction in accordance with the equation



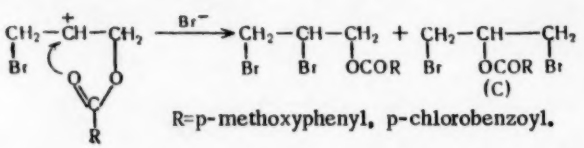
in which ROH is the solvent.

In this connection we must mention the work [14], which showed that hypochlorous acid adds normally to allyl alcohol and to allyl chloride with formation of a mixture of "glycerol chlorohydrins":



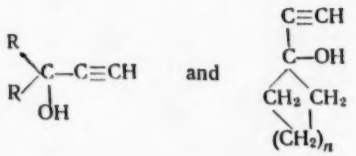
in which X = OH, Cl.

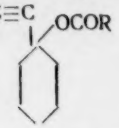
Quite recently a short communication has appeared [15] on the bromination of allyl esters, and in this a reaction mechanism is examined for bromination with bromine in chloroform which admits of the possibility of the participation of the carbonyl group of the acyl group of a weak acid in the bromination reaction. This provides an explanation of the formation of anomalous bromination products (C):



R=p-methoxyphenyl, p-chlorobenzoyl.

In view of the above discussion, it is still impossible to provide a satisfactory explanation, on the basis of a single unified mechanism, of all our results. The question may be clarified somewhat by a study of infrared and Raman spectra of acetylenic alcohols and their acetates. It is interesting that the data available in the literature on this matter are in good agreement with the results of our chemical experiments. As was shown recently [16], tertiary acetylenic alcohols of general formulas



show very weak absorption in the triple bond region (2200-2100 cm^{-1}), though there is a strong ≡C–H frequency in the 3300-3200 cm^{-1} region. On the other hand, 1-ethynylcyclohexanol m-bromobenzoate 

has a line of medium intensity in the region of 2103 cm^{-1} (with strong ≡C–H absorption displaced from 3265 cm^{-1} for the free OH group to 3235 cm^{-1} for the ester).

2-Propyn-1-ol (primary OH group) has a line of medium intensity at 2100 cm^{-1}, but 1-heptyn-3-ol (secondary OH group) has a weak line at 2080 cm^{-1}. These results indicate interaction between the terminal acetylenic group and a tertiary hydroxyl conjugated with it. In its turn, this affects the mechanism of the reaction of hypobromous acid with multiple bonds of acetylenic (and possibly ethylenic) alcohols and their acetates. It is probably this, together with the reaction conditions, that explains the observed difference in the stereochemistry of the addition of halogens to the multiple bonds of acetylenic alcohols and their acetates. We shall deal with this question in greater detail in another place.

EXPERIMENTAL

1-(trans-1,2-Dibromovinyl)-cis-2-methylcyclohexanol (VII). A solution of hypobromous acid was prepared from 50 g of acetamide, 100 g of bromine, 50 g of sodium acetate, and 40 ml of glacial acetic acid by the method which we have described previously [3]. To the dark-red clear solution so obtained, an acetic acid solution of 20 g of the cis alcohol (V) was added with stirring over a period of 30 minutes. Reaction was accompanied by slight rise of temperature (from 12° to 24°). A dark-red oil was precipitated. The solution was neutralized with sodium bicarbonate, and the reaction product was extracted with ether; the extract was dried with sodium sulfate. Vacuum fractionation gave 13.5 g of 1-(trans-1,2-dibromovinyl)-cis-2-methylcyclohexanol (VII) as a faintly yellow thick liquid which darkened when allowed to stand in air; b.p. 115-116° (4 mm); n_D^{20} 1.5574; d_4^{20} 1.6822; found MR 57.76; calculated MR 58.15. Found: C 36.04; 36.21; H 4.80; 4.80; Br 53.26; 53.50%. $C_9H_{14}OBr_2$. Calculated: C 36.26; H 4.71; Br 53.66%.

Debromination of the cis alcohol (VII) by boiling it with zinc dust in acetic acid gave the original alcohol (V), which gave the characteristic reaction for acetylenic hydrogen with ammoniacal silver nitrate.

1-(trans-1,2-Dibromovinyl)-trans-2-methylcyclohexanol (VIII). trans-1-Ethynyl-2-methylcyclohexanol (VI) (20 g) was added to a stirred hypobromous acid solution prepared from 50 g of acetamide and 100 g of bromine by the method referred to above. Reaction was accompanied by slight evolution of heat. A dark-red oil was precipitated. After the usual treatment (see previous experiment) and vacuum fractionation of the reaction products we obtained about 20 g of 1-(trans-1,2-dibromovinyl)-trans-2-methylcyclohexanol (VIII) as a thick, almost colorless liquid which gradually darkened when allowed to stand; b.p. 114-115.5° (4 mm); n_D^{20} 1.5565; d_4^{20} 1.6522; found MR 57.95; calculated MR 58.15. Found: C 36.37; 36.16; H 4.82; 4.83; Br 53.43; 53.02%. $C_9H_{14}OBr_2$. Calculated: C 36.26; H 4.71; Br 53.66%.

Debromination of the trans alcohol (VIII) in the way described above gave the original trans alcohol (VI), which gave the characteristic test for acetylenic hydrogen with ammoniacal silver nitrate. The bromination of the trans alcohol (VI) goes more smoothly.

trans-2,3-Dibromo-2-propen-1-ol (X). 2-Propyn-1-ol (IX) (b.p. 110-113.5°; n_D^{20} 1.4300; 25g; prepared by the extraction of a 33% aqueous solution with ether) [17] was added to a solution of hypobromous acid prepared as described above from 50 g of acetamide and 100 g of bromine. The usual treatment and vacuum fractionation gave about 40 g of crude (X). Further vacuum fractionations gave 20 g of trans-2,3-dibromo-2-propen-1-ol (X) as a heavy colorless liquid; b.p. 86° (7 mm); n_D^{20} 1.5793; d_4^{20} 2.2132; found MR 32.42; calculated MR 34.64. Found: C 17.03; 17.06; H 1.94; 2.02; Br 72.82; 72.51%. $C_3H_4OBr_2$. Calculated: C 16.68; H 1.85; Br 74.05%.

Debromination of the alcohol (X) in the way described above gave the original 2-propyn-1-ol (IX), which gave the characteristic reaction for acetylenic hydrogen with ammoniacal silver nitrate.

2-Propyn-1-ol Acetic Ester (XI). 2-Propyn-1-ol (IX) (35 g; b.p. 113-113.5°; n_D^{19} 1.4328) was acetylated with 100 g of acetic anhydride in presence of one drop of concentrated sulfuric acid with cooling.

On the next day the solution was heated for two hours at 70°. The solution was cooled, diluted with water, and neutralized with sodium bicarbonate. The acetic ester was extracted with ether. The ether extract was

dried with sodium sulfate, ether was distilled off, and the residue (about 70 g) was fractionated. We obtained 52 g (83%) of 2-propyn-1-ol acetic ester [17] as a colorless liquid, b.p. 123-125° and n_D^{19} 1.4200.

trans-2,3-Dibromo-2-propen-1-ol Acetic Ester (XII). Over a period of five minutes, 20 g of the acetic ester of (XI) (b.p. 123-125°; n_D^{19} 1.4200) was added to a solution of hypobromous acid prepared from 50 g of acetamide and 100 g of bromine as described above. The temperature of the reaction mixture rose from 8° to 21°. The flask was cooled with cold water. The heavy oily reaction product was extracted with ether, and the extract was neutralized with sodium bicarbonate solution and dried with sodium sulfate. Ether was distilled off, and vacuum fractionation gave trans-2,3-dibromo-2-propen-1-ol acetic ester (XII) as an almost colorless liquid; b.p.89.5-91° (7 mm); n_D^{20} 1.5258; d_4^{20} 1.8837; found MR 41.49; calculated MR 42.0. Found: C 23.52; 23.70; H 2.33; 2.41; Br 61.52; 61.59%. $C_5H_6O_2Br_2$. Calculated: C 23.33; H 2.33; Br 61.99%.

2-Butyne-1,4-diol Diacetate (XV). A solution of 75 g of freshly distilled 2-butyne-1,4-diol (XIV) (m.p. 57°) in 254 g of freshly distilled acetic anhydride was heated to 120-130° in three hours. A rise in the temperature of the solution to 140-150° was observed, and this was accompanied by vigorous boiling of the liquid for about ten minutes. The yellow solution was left overnight. On the next day excess of acetic anhydride was distilled off and the residue was vacuum-fractionated. We obtained 148 g of the diacetate (XV) as a colorless liuqid, b.p. 116-118° (8 mm) and n_D^{20} 1.4540; the yield was almost quantitative. When cool, the diacetate crystallized in colorless crystals, m.p. 27-28°. The literature [7] gives m.p. 28°.

2,3-Dibromo-2-butene-1,4-diol (XVII). A solution of 20 g of the butynediol (XIV) in 35 ml of glacial acetic acid was added to a solution of hypobromous acid prepared by the above-described method from 50 g of acetamide and 106 g of bromine. The reaction was exothermic. On neutralization of the clear solution with solid sodium bicarbonate there was a precipitate of colorless crystals [10] of 2,3-dibromo-2-butene-1,4-diol (XVII), m.p. 113-114° (from diethyl ether + petroleum ether); yield 33 g. Found: C 19.59; 19.64; H 2.50; 2.66; Br 64.61; 64.79%. $C_4H_6O_2Br_9$. Calculated: C 19.53; H 2.44; Br 65.02%.

The dibromo compound (XVII) of m.p. 113-114° was prepared also by the bromination of the butynediol (XIV) with bromine in glacial acetic acid (ionic addition [6]). Reaction was exothermic. The literature [10] gives m.p. 117°. When the butynediol (XIV) was brominated with bromine in a mixture of chloroform and carbon tetrachloride in the light (nonionic addition [6]), no crystalline reaction products were isolated.

2,3-Dibromo-2-butene-1,4-diol Diacetate (XVIII). Preparation by reaction of hypobromous acid with butynediol diacetate (XV): with cooling, 30 g of the diacetate (XV) in 40 ml of glacial acetic acid was added over a period of ten minutes to a solution of hypobromous acid prepared from 50 g of acetamide and 106 g of bromine. After five minutes the homogeneous solution frist became turbid and then gave a red oily precipitate. The temperature of the solution rose from 9° to 25°. To bind the excess of bromine ions dry thiosulfate was added until the mixture was decolorized (about 10 g), and the solution was neutralized with sodium bicarbonate. The almost colorless oil (about 70 g) which was then precipitated was separated and dissolved in ether. The ether solution was dried with sodium sulfate, and vacuum fractionation gave about 50 g (80%) of 2,3-dibromo-2-butene-1,4-diol diacetate (XVIII) as a thick lemon-yellow liquid, b.p. 154-155° (7 mm) and n_D^{20} 1.5125, which crystallized when cool to colorless crystals, m.p. 60-60.5° (from petroleum ether). Found: C 29.38; 29.36; H 3.09; 3.29; Br 48.38; 48.30%. $C_8H_{10}O_4Br_2$. Calculated: C 29.11; H 3.03; Br 48.47%.

Acetylation of 2,3-dibromo-2-butene-1,4-diol (XVII) with acetyl chloride: Acetyl chloride (5.5 ml) was added to 2.5 g of the dibromo compound (XVII), m.p. 113-114°, in 40 ml of ether (partial dissolution), and the mixture was refluxed for five hours. On the next day the colorless solution was vacuum-evaporated, and the residue was crystallized from petroleum ether. This gave 2 g of the diacetate (XVIII), m.p. 60-60.5°, undepressed by admixture of the sample described above.

2,3-Dibromo-1,4-dichloro-2-butene (XIX). Reaction of hypobromous acid with 1,4-dichloro-2-butyne (XVI): 1,4-Dichloro-2-butyne (XVI) (15 g; b.p. 68° (22 mm); n_D^{20} 1.5040; prepared from the butynediol (XIV) by the action of thionyl chloride) was added to a solution of hypobromous acid prepared from 10 g of acetamide and 52 g of bromine (see preceding experiments). After some time a crystalline product was precipitated. On the next day the crystals were filtered off and recrystallized from petroleum ether. This gave 35 g of 2,3-dibromo-1,4-dichloro-2-butene (XIX) in the form of colorless crystals, m.p. 59.5-60°, which had a powerful lacrimatory action. Found: C 16.91; 17.08; H 1.39; 1.49; Cl + Br 81.30; 81.62%. $C_4H_4Cl_2Br_2$. Calculated: C 16.98; H 1.41; Cl+Br 81.61. The literature [10] gives m.p. 58°.

Addition of bromine to 1,4-dichloro-2-butyne (XVI) in carbon tetrachloride: Bromine (6.5 g) was added to a solution of 5 g of the dichlorobutyne (XVI) in 80 ml of dry carbon tetrachloride. The reaction was slightly exothermic. After one hour solvent was vacuum-distilled off. The residue crystallized out almost completely. Recrystallization from a mixture of diethyl ether and petroleum ether gave 3 g of crystals of the above-described dibromodichloro-2-butene (XIX), m.p. 59.5-60°, undepressed by admixture of the analyzed sample. In addition we obtained a mother liquid which partially crystallized; it was not investigated further.

Bromination of 1-Ethynylcyclohexanol Acetate with Bromine in Aqueous Methanol. With stirring and cooling with water, 45 g of bromine was added over a period of 30 minutes to a solution of 25 g of 1-ethynylcyclohexanol acetate [b.p. 66-67° (3 mm), n_D^{21} 1.4667] in 150 ml of methanol [18] and 20 ml of water. The reaction was exothermic. The colored solution was diluted with water. A heavy red oil was precipitated, and this gradually crystallized. The crystals were filtered off and recrystallized from petroleum ether. We obtained 33 g (65%) of the known [3] 1-(2,2-dibromoacetyl) cyclohexanol acetate, m.p. 53-54°, undepressed by admixture of a known sample.

SUMMARY

1. A study was made of the reactions of hypobromous acid with cis- and trans-1-ethynyl-2-methylcyclohexanols, 2-propyn-1-ol and its acetate, 2-butyne-1,4-diol and its diacetate, and 1,4-dichloro-2-butyne.

2. In all these cases the course of the reaction of hypobromous acid with the triple bond was anomalous and led to the formation of the corresponding unsaturated dibromo compounds, which were probably of trans configuration. Some of these products were prepared also by bromination of the original acetylenic compounds with bromine in nonpolar solvents in the light.

3. A hypothesis is advanced concerning the effect of a neighboring hydroxy or acetoxy group on the character of the reaction of hypobromous acid with the triple bond.

4. In the bromination of 1-ethynylcyclohexanol acetate with bromine in aqueous methanol normal addition of hypobromous acid to the triple bond occurs and the known 1-(2,2-dibromoacetyl) cyclohexanol acetate is isolated in 65% yield.

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*Original Russian pagination. See C.B. translation.

CATALYTIC POLYMERIZATION OF OLEFINS

COMMUNICATION 7. POLYMERIZATION OF ETHYLENE OVER A NICKELOUS OXIDE - ALUMINUM SILICATE CATALYST

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It was shown previously [1] that alumina has a powerful promoting effect on a nickelous oxide - silica gel (KSK) catalyst for the polymerization of ethylene. On the other hand, various clays were investigated and found to be unsuitable as a carrier for the nickel catalyst in this reaction. It was of interest to examine the behavior of synthetic aluminum silicates in this respect.

In the literature [2] there is a description of the polymerization of ethylene in admixture with hydrogen at 40° and 20 atm over an NiO catalyst carried by a synthetic cracking aluminum silicate. The conversion of ethylene was about 97%; the yield of polymer, which contained 50% of butenes, was 325 g/liter·hr.

In the present work we studied the following samples of synthetic aluminum silicates in tablet form: a Houdry cracking catalyst (I), an analogous treating catalyst (II), and a Soviet aluminum silicate cracking catalyst (III) [3]. The physical properties and chemical compositions of these aluminum silicates have been given previously [4]. The apparatus and experimental procedure were as before [5]. The experiments were carried out at 300° with catalysts prepared both by precipitation from nickel nitrate and by impregnation with nickel formate. Each experiment, when continuous, lasted for five hours.

EXPERIMENTAL

Precipitated NiO - Aluminum Silicate (Tablet Form) Catalysts. The following catalysts were used: Catalyst 88 had a carrier of aluminum silicate I in tablet form; precipitation was carried out with aqueous ammonia from saturated nickel nitrate solution (15 ml per 10 ml of aluminum silicate). Catalyst 86 differed from Catalyst 88 only in that precipitation was carried out with potassium carbonate.

The results obtained with these catalysts at a time of contact of 11-12 seconds are given in Table 1. This table shows that with Catalyst 88, which was prepared by precipitation with ammonia, the yield of dimer averaged at 35.4% on the ethylene passed and 53.5% on the ethylene that reacted. After 15 hours of work the conversion of ethylene fell from 80% to 54%; there was a simultaneous fall in the yield of higher hydrocarbons. After regeneration in a stream of air at 450°, the catalyst worked further for 20 hours with almost the same activity, and the same regularities were observed as regards the change in the amount of ethylene that reacted and the fall in the yield of liquid condensate. Catalyst 86, prepared by precipitation with potassium carbonate, was more selective with respect to dimerization: the yield of dimer was 43.3-30.7% on the ethylene passed and 63.6-78.8% on the ethylene that reacted; the yield of higher hydrocarbons was less than in the experiments with Catalyst 88. However, after regeneration Catalyst 86 lost its selectivity. It is interesting that the yield of higher hydrocarbons was greater over a fresh catalyst and immediately after regeneration than in subsequent experiments.

TABLE 1

Activities of Precipitated NiO - Aluminum Silicate (Tablet Form) Catalysts

Catalyst No.	Catalyst	Expt.	Ethylene that reacted (%)	Yield of butene (% on ethylene passed)	Yield of butene (% on ethylene that reacted)	Yield of butene (g/liter of catalyst per hour)	Yield of higher hydrocarbons (%) on ethylene passed	Yield of higher hydrocarbons (%) on ethylene that reacted
88	NiO–aluminum silicate (for cracking), precipitated with ammonia	1—3	80,0—54,0	35,4	53,5	145—136	23,3—10,3	29,1—19,1
		4*—7	82,0—53,4	32,9	47,5	147—96	26,2—7,5	32,0—14,0
88	The same							
86	NiO–aluminum silicate (for cracking), precipitated with potassium carbonate	1—2	68,0—39,0	43,3—30,7	63,6—78,8	200—130	17,5—7,2	25,8—18,5
		3*	49,4	27,9	56,5	120	12,0	24,3
86	The same							

* Before this experiment the catalyst was regenerated in a stream of air at 450° for five hours.

Impregnated NiO - Aluminum Silicate (Tablet Form) Catalysts. Catalyst 77 had aluminum silicate I as carrier. Impregnation was carried out with a boiling 1% solution of nickel formate. Catalyst 100 differed from Catalyst 77 only in that the carrier was aluminum silicate II. Catalysts 107 and 200 were identical with the previous catalysts, but aluminum silicate III in tablet form was used as carrier; in the analogous Catalyst 99, tablets of aluminum silicate III were first ground to a powder. In the experiments with Catalyst 200 the time of contact was 6 seconds, and in work with the other catalysts the time was 11-12 seconds.

The results are presented in Table 2.

Table 2 shows that Catalyst 77 was distinguished by its good regenerability but low selectivity for the dimerization of ethylene. Catalyst 100 could also be regenerated satisfactorily. As the amount of work done by this catalyst increased, its selectivity increased. Catalyst 107 was found to be less active, poorly regenerable, and of low selectivity. The results obtained with Catalyst 99 show that the use of the carrier in powder form results in lower activity and stability. Comparison of the results of the work of Catalysts 107 and 200 shows that, with reduction of the contact time to one-half, the total conversion of ethylene is reduced by more than one half, though the yield of dimer on the amount of ethylene that reacts increases, i.e., the selectivity of the catalyst for dimerization increases. However, after the second regeneration the selectivity of the catalyst fell sharply.

The impregnated catalyst was tested in prolonged work with overnight interruptions and recirculation of ethylene, and also in prolonged uninterrupted work. All these experiments were carried out with a contact time of 9-12 seconds.

Work with Interruptions Between Experiments. Catalyst 76 was used; this differed from Catalyst 77 only in that impregnation of the aluminum silicate was with a saturated nickel formate solution. The results are shown in Figures 1 and 2. Eleven regenerations were carried out in 95 hours. During the whole working period, 365 liters of ethylene was passed and, on the average, 52.5% of this reacted. The average yield of dimer was 32.7% on the ethylene passed and 58% on the amount that reacted. The yield of higher hydrocarbons was 13.5% and 22.9%, respectively. After about 100 hours of contact the catalyst largely maintained its activity, even after the eleventh regeneration.

Experiments with Recirculation of Gas. In this series of experiments we used Catalyst 135, which is like Catalyst 77. The results obtained with this catalyst are given in Table 3. In 50 hours 99.3 liters of 99% ethylene was passed; we obtained 10.5 liters of composition

TABLE 2

Activities of Impregnated NiO - Aluminum Silicate (Tablet Form) Catalysts

Catalyst No.	Catalyst	Expt.	Ethylene that reacted (%)	Yield of butene (% on ethylene passed)	Yield of butene (% on ethylene that reacted)	Yield of butene (g/liter of catalyst per hour)	Yield of higher hydrocarbons (%) on ethylene passed	Yield of higher hydrocarbons (%) on ethylene that reacted
77	Aluminum silicate (for cracking)	1—3	77,0—54,2	41,0—23,6	58,8—43,5	137—70	26,7—14,0	34,8—25,1
77	The same	4*	70,4	31,9	45,3	114	20,0	28,5
100	Aluminum silicate (for treating)	1—3	89,0—47,0	21,6—39,2	24,2—72,6	81—197	35,2—11,2	39,3—22,6
100	The same	4*—6	76,0—58,1	40,0—35,8	52,6—61,0	151—137	24,6—9,0	32,4—15,4
100	" "	7*—9	69,7—42,9	37,8—22,4	54,3—59,2	140—89	21,2—5,0	30,5—13,5
107	Aluminum silicate (Soviet)	1—2	66,7—45,4	35,4—26,3	53,9—57,9	144—100	20,7—7,8	31,0—17,2
107	The same	3*	29,2	20,7	70,8	88	6,3	21,6
107	" "	4*	35,7	17,2	48,3	79	8,1	23,8
107	" "	5*	26,1	15,5	59,5	79	4,4	16,9
99	The same (powder)	1—2	49,7—20,9	29,3—5,3	58,8—25,4	128—21	5,1—2,1	10,2—10,1
99	" "	3*	12,0	5,0	41,6	25	2,0	16,6
200	Aluminum silicate (Soviet)	1—2	28,9—19,3	20,4—13,7	70,3—71,0	162—108	5,5—2,8	19,2—14,6
200	The same	3*	7,7	7,6	98,5	59	1,1	13,8
200	" "	4*—5	26,8—6,9	12,4—2,8	46,6—41,0	82—22	4,2—0,7	15,8—9,9

*Before this experiment the catalyst was regenerated in a stream of air at 450° for five hours.

TABLE 3

Experiments with Recirculation of Gas

Expt.	Original gas (liters)		Contraction (%)	Yield of butene			Yield of higher hydrocarbons (%)	
	fresh	returned into the reactions		(% on ethylene passed)	% on ethylene that reacted	(g/liter of catalyst per hour)	on ethylene passed	on ethylene that reacted
1	19,1	0,0	75,3	37,6	50,0	180	22,9	30,4
2	15,3	4,7	54,2	27,3	50,3	130	5,4	10,0
3	12,5	6,4	49,2	31,7	64,4	150	6,3	12,8
4*	9,7	9,6	62,7	37,3	59,4	180	8,6	13,7
5	12,1	7,2	36,7	20,7	56,3	100	5,9	16,0
6*	6,8	12,2	50,0	25,2	50,4	140	11,3	22,6
7	9,4	9,5	32,6	15,8	52,4	75	4,4	14,6
8*	5,9	13,2	47,1	25,1	53,2	120	12,0	25,4
9	8,9	10,1	26,3	15,7	59,7	75	3,5	13,3
10**	0,0	14,0	36,0	17,6	49,0	60	8,2	22,8
11***	0,0	8,7	16,6	9,5	57,0	20	—	—

*Before this experiment the catalyst was regenerated in a stream of air at 450° for 5 hours.

**Expt. 10 lasted for 3.5 hours.

***Expt. 11 lasted for 2.3 hours.

73.1% C_2H_4, 1.8% CO, 3.5% H_2, and 21.6% ($Cn\ H_{2n+2} + N_2$). The ethylene reacted to the extent of 88.8%. The yield of dimer was, on the average, 49.9% on the ethylene passed and 54.5% on the ethylene that reacted. The yield of higher hydrocarbons was 16.6% and 18.1%, respectively. In the whole working period the catalyst was regenerated three times.

Continuous Processing. In these experiments, which were carried out continuously (no overnight interruption), we used Catalyst 133, which was in all respects similar to Catalyst 135. The results are given in Fig. 3.

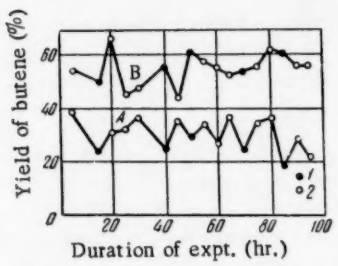

Fig. 1. Yield of butene in prolonged working of NiO - aluminum silicate (tablet form) catalyst (Catalyst 76): 1) Experiment with unregenerated catalyst; 2) experiment just after regeneration; A) yield (% on ethylene passed); B) yield (% on ethylene that reacted).

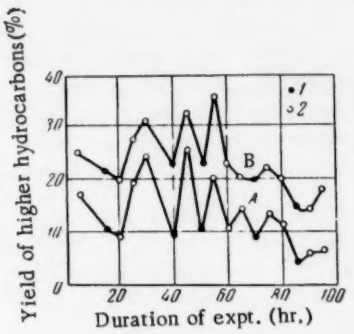

Fig. 2. Yield of higher hydrocarbons in prolonged work of NiO - aluminum silicate (tablet form) catalyst (Catalyst 76): 1) Experiment with unregnerated catalyst; 2) experiment just after regeneration; A) yield (% on ethylene passed); B) yield (% on ethylene that reacted).

In 108.5 hours, 413.4 liters of ethylene was passed. The average gas contraction was 44.2%. The yield of dimer was 27% on the ethylene passed and 61.1% on the ethylene that reacted. The yield of higher hydrocarbons was 6.0% on the ethylene passed and 13.5% on the ethylene that reacted.

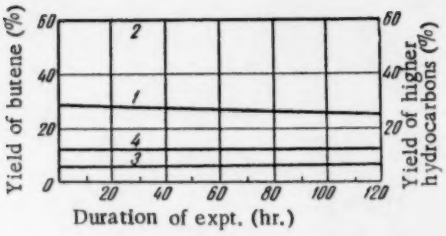

Fig. 3. Yields of butene and higher hydrocarbons in continuous working (Catalyst 133): 1) yield of butene (% on ethylene passed); 2) yield of butene (% on ethylene that reacted); 3) yield of higher hydrocarbons (% on ethylene passed); 4) yield of higher hydrocarbons (% on ethylene that reacted).

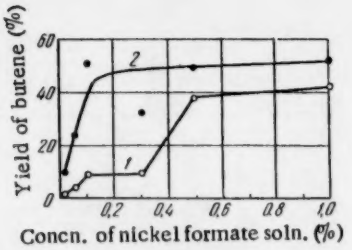

Fig. 4. Effect of the concentration of the nickel formate solution on the activity of the catalyst: 1) yield of butene (% on ethylene passed); 2) yield of butene (% on ethylene that reacted).

Effect of the Concentration of the Solution of Nickel Salt on the Properties of an Impregnated Catalyst.

It is well known that the conditions under which a catalyst is prepared greatly affect its activity. This is often applicable to the concentrations of the solution used in the preparation of the catalyst. It was of interest to determine the effect of the concentration of the nickel formate solution used for the impregnation of the carrier. In these experiments, tablet-form aluminum silicate I was used. The concentrations of the solutions used were 0.01, 0.05, 0.1, 0.3, 0.5, and 1%. The length of the catalyst layer was 16 cm. The results are shown in Fig. 4. It was found that, within the limits of the range of nickel formate solutions (0.01-1.0%) investigated, the activity and productivity of the catalyst increase with rise in this concentration. At concentrations of less than 0.3% the catalysts obtained are of low activity and low productivity. Only at concentrations of 0.3% and higher do the activity and productivity rise.

In the study of the activity of the aluminum silicate for the polymerization of ethylene we used Catalyst 89, which consisted of aluminum silicate I in tablet form. The catalyst was found to be quite inactive for the polymerization of ethylene.

To investigate the replacement of nickel in a nickelous oxide - aluminum silicate (tablet form) catalyst by cobalt, iron, or copper, we prepared a catalyst in which cobalt was precipitated from its nitrate with ammonia on aluminum silicate, one in which aluminum silicate was impregnated with ferric nitrate, and one in which aluminum silicate was impregnated with copper formate. In all these the carrier was aluminum silicate I. The length of the catalyst layer was 18 cm. All these catalysts were found to be quite inactive. Neither dimer nor polymer was obtained in their presence. Hence, when nickel is replaced by iron, cobalt, or copper, catalysts are obtained which are inactive for the polymerization of ethylene.

To determine the effect of treatment of the aluminum silicate with alkali on the properties of an NiO - aluminum silicate catalyst we used Catalyst 119 (aluminum silicate I carrier, impregnated with formate) which had been previously treated with boiling 2% potassium hydroxide solution. The catalyst was quite inactive for the polymerization of ethylene. This is in good agreement with views relating to the activity of hydrogen ions in the aluminum silicate structure.

Examination of the results obtained in this investigation shows that an NiO - aluminum silicate (tablet form) catalyst has a high polymerizing power, as a result of which its selectivity for dimerization is low compared with that of NiO - Al_2O_3 - silica gel (KSK), in which the aluminum silicate phase is considerably smaller in extent. Aluminum silicate, which is active in the polymerization of propene [6] and butene [7], showed no activity in the same reaction of ethylene, though when NiO was introduced it became active in this reaction also. However, the introduction of Co, Cu, or Fe oxides did not have this effect. This is particularly noteworthy since a Co - charcoal catalyst is active in the dimerization of ethylene [8]. The view that aluminum silicate is an active component of the catalyst, which was developed in the proceding communication [1], and also the view that we are here dealing with a complex variety of acid catalysis, is confirmed by the fact that alkali completely deactivates an NiO - aluminum silicate catalyst.

SUMMARY

1. Nickelous oxide - synthetic aluminum silicate (tablet form) catalysts prepared by precipitation or impregnation show considerable activity for the polymerization of ethylene at 300° and atmospheric pressure. Aluminum silicate is not itself a catalyst in this reaction.

2. When nickel is replaced by iron, cobalt, or copper in a nickelous oxide - aluminum silicate catalyst, the products are inactive for the polymerization of ethylene.

3. Aluminum silicate that has been treated with a solution of alkali is unsuitable as a carrier for nickelous oxide; this is in good agreement with the view of the activity of hydrogen ions in an aluminum silicate.

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HIGHLY ACTIVE NICKEL – ALUMINA CATALYST FOR THE DEHYDROGENATION OF THE CYCLOHEXANE RING

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Since Sabatier and Senderens's first classical investigations [1], nickel has been rightly regarded as one of the best hydrogenation catalysts among the nonnoble metals. During the period of their development the theory and practive of heterogeneous catalysis provided many examples of active nickel catalysts for the hydrogenation of various organic compounds, including aromatic compounds. However, whereas nickel is a good catalyst for the gas-phase hydrogenation of the aromatic nucleus, in the reverse reaction, i.e., the dehydrogenation of the cyclohexane ring, it behaves in an extremely peculiar manner. Thus, many nickel catalysts are known which are always highly active for the hydrogenation of the benzene nucleus, but cannot effectively bring about the dehydrogenation of cyclohexanes at 300°. These include: a) catalysts prepared by precipitation from solutions of nickel and aluminum salts with sodium or potassium carbonate solution with the aim of simultaneous formation of the carrier [2]; b) catalysts prepared by the impregnation of the carrier (asbestos) with concentrated nickel nitrate solution with subsequent drying and mild roasting [3]; c) Raney catalysts prepared from alloys of nickel with aluminum or zinc [4].

As Sabatier, Maihle, and Senderens showed [5], pure nickel (no carrier) reduced from nickelous oxide is also unsuitable for the dehydrogenation of the cyclohexane ring because at 270° and above it acquires a very pronounced aggressive character. The nickel-alumina catalyst described by Pfaff and Brunck [6] must also be included in the group of catalysts which actively promote hydrogenation, but are unable to accelerate dehydrogenation.

Up to now essentially the only nickel dehydrogenation catalyst is that proposed by Zelinskii and Komarevskii [7]: it consists of nickel deposited on alumina. This catalyst differs from that of Pfaff and Brunck in that in its preparation a portion of alumina containing some hydration water ($Al_2O_3 \cdot H_2O$) is added to the combined precipitate of nickelous and aluminum hydroxides. In this way finely dispersed nickel formed after the reduction of the "raw" catalyst is distributed on a heterogeneous catalyst: hydrous alumina formed from freshly precipitated hydroxide and alumina introduced into the catalyst (in the form of small pieces) after the ingredients of the catalyst had already been precipitated.

As the results of these same authors [7] and the investigations of one of us with Zelinskii [8] and Balandin [9] show, this catalyst is highly active in many cases for the dehydrogenation of the cyclohexane ring. However, it must be pointed out that the method for the preparation of this catalyst described by Zelinskii and Komarevskii does not guarantee its production with definite properties that are always reproducible, a fact which we frequently confirmed in a study of a series of catalysts of this type [10]. The lack of reproducibility of the properties of the catalyst prepared by Zelinskii and Komarevskii's method was shown in the present work for the case of Catalysts 4 and 5, which were prepared under identical conditions by this method and reduced under strictly identical conditions with electrolytic hydrogen. The catalysts differed greatly in ability to promote the dehydrogenation of cyclohexane: Catalyst 4 was of low activity. A similar sharp difference in the properties of three samples of an analogous catalyst was observed also by Rubinshtein [11], who determined the dispersity

TABLE 1

Initial Activities of Nickel-Alumina Catalysts for the Dehydrogenation of Cyclohexane at 300° at a Space Velocity of 0.4 $hour^{-1}$

Catalyst No.	Catalyst	n_D^{20} of catalyzate	Conversion into benzene %
4	Ni–Al_2O_3 according to Zelinskii and Komarevskii (56%) Ni)	1.4554	48.2
5	The same	1.4907	90.0
6	50% Ni + 50% Al_2O_3 according to our improved method	1.4939	93.4
8	30% Ni + 70% Al_2O_3 according to our improved method	1.4975	97.0

TABLE 2

Duration of Work of Catalysts 4 and 5 in the Dehydrogenation of Heptane-Methylcyclohexane Fractions of Surakhan and Maikop Gasolines

Catalyst No.	Substance being dehydrogenated	Time from start of work (min.)	Properties of catalyzates		
			n_D^{20}	conversion of cyclohexane into benzene (%)	toluene content (% by vol.)
4	Cyclohexane	5	1.4775	75.8	–
	98-103° fraction of Surakhan gasoline	115	1.4318	–	25.0
	The same	192	1.4267	–	18.0
	Cyclohexane	197	1.4546	47.4	–
	Total: 3 hr. 17 min.				
5	Cyclohexane	5	1.4907	90.0	–
	97-103° fraction of Maikop gasoline	750	1.4383	–	42.0
	Cyclohexane	755	1.4633	58.6	–
	97-103° fraction of Maikop gasoline	1275	1.4269	–	28.0
	Cyclohexane	1280	1.4600	54.8	–
	97-103° fraction of Maikop gasoline	2250	1.4260	–	26.0
	Cyclohexane	2250	1.4517	43.4	–
	Regeneration I				
	Cyclohexane	2250	1.4900	89.2	–
	97-103° fraction of Surakhan gasoline	2335	1.4375	–	45.0
	97-103° fraction of Surakhan gasoline	4875	1.4302	–	32.0
	Cyclohexane	4880	1.4585	53.6	–
	98-103° fraction of Maikop gasoline	5400	1.4270	–	28.0
	Cyclohexane	–	1.4517	43.4	–
	Regeneration II				
	Cyclohexane	5405	1.4693	67.0	–
	97-103° fraction of Maikop gasoline	7000	1.4260	–	26.5
	Cyclohexane	7005	1.4575	51.3	–
	Total: 116 hr. 45 min.				

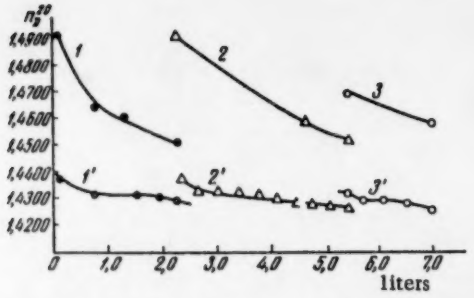

Fig. 1. Relation of the activity of Catalyst 5 toward cyclohexane and toward gasoline to the amount of aromatized gasoline: 1) and 1') cyclohexane and gasoline-fraction catalyzates before the regeneration of the catalyst; 2) and 2') cyclohexane and gasoline-fraction catalyzates after the first regeneration of the catalyst; 3) and 3') cyclohexane and gasoline-fraction catalyzates after the second regeneration.

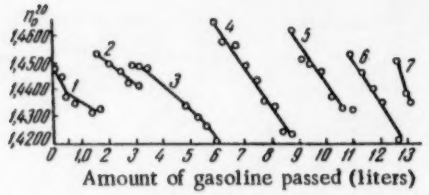

Fig. 2. Relation of the activity of Catalyst 6 to the amount of aromatized gasoline: 1) gasoline catalyzates before regeneration of catalyst; 2) gasoline catalyzates after first regeneration of catalyst; 3) gasoline catalyzates after second regeneration of catalyst; 4) gasoline catalyzates after third regeneration of catalyst; 5) gasoline catalyzates after fourth regeneration of catalyst; 6) gasoline catalyzates after fifth regeneration of catalyst; 7) gasoline catalyzates after sixth regeneration of catalyst.

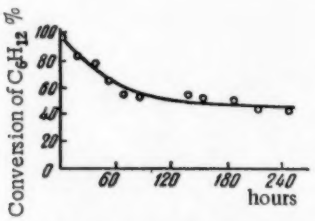

Fig. 3. Change in the activity of Catalyst 8 toward cyclohexane in the aromatization of unfractionated Surakhan gasoline.

of nickel in these samples and found it to be, respectively, 102 A (Catalyst 6), 85.5 A (Catalyst 5), and 73 A (Catalyst 4). On the basis of activity-dispersity isotherms they showed that only two samples (Catalysts 12 and 13) had close to the optimum dispersity, which lay in the range 75-80 A.

Also, some of the procedures used in the preparation of Zelinskii and Komarevskii's catalyst are essentially erroneous. These include the enormous excess of nickel (145 g) which, after preliminary conversion into nitrate, is taken for the preparation of the catalyst: only 175 g of aluminum nitrate, which contains nine molecules of water of crystallization, is taken in the precipitation reaction; calculation shows that only 13.7 g (i.e., 9.5%) of the nickel can be precipitated (from the nitrate solution) as nickelous hydroxide under the conditions described by the authors. From this it is clear also that the presence of excess of nickel nitrate in the reaction mixture obtained after precipitation makes its treatment with carbon dioxide, as recommended by the authors, unnecessary. It follows from the above discussion that for the dehydrogenation of the cyclohexane ring a nickel catalyst having reproducible properties has not yet been found. Some data on the effect of individual factors (natures of carrier and precipitant and the presence of impurites) determining the activity and stability of nickel dehydrogenation catalysts were obtained by Gaverdovskaya [12].

Having set outselves the task of finding conditions for the preparation of an active and stable dehydrogenating catalyst having reproducible properties, we decided to examine some of the factors concerned in the preparation of the catalysts and having a determining effect on their ability to promote dehydrogenation. Our investigation [10] showed that in the given case such factors as the composition of the original salts, the chemical nature of the precipitants, and the character and conditions of precipitation have a substantial effect in determining the structure and properties of the catalysts. By a combination of these factors under various conditions we have succeeded in obtaining precipitates of nickelous hydroxide which, when reduced with hydrogen in accordance with a definite temperature schedule, gave a highly active dehydrogenating catalyst in which the nickel appeared to have optimum dispersity. According to Rubinshtein's observations [11], the latter is one of the important factors determining the activity of a catalyst in various reactions and also its specificity.

TABLE 3

Duration of Work of Catalysts 6 and 8 in the Dehydrogenation of Heptane -Methylcyclohexane Fractions of Various Gasolines and of Unfractionated Surakhan Gasoline

Catalyst No.	Substance being dehydrogenated	Time from start of work(min.)	Properties of catalyzates		
			n_D^{20}	conversion of cyclohexane into benzene(%)	toluene content (% by vol.)
6	Cyclohexane	5	1.4939	93.4	–
	98-103° fraction of Surakhan gasoline	1000	1.4350	–	32.5
	The same	1650	1.4330	–	30.0
	Cyclohexane	1655	1.4665	63.2	–
	Regeneration I				
	Cyclohexane	1660	1.4930	92.6	–
	98-103° fraction of Surakhan gasoline	3000	1.4435	–	42.0
	Cyclohexane	3005	1.4620	57.5	–
	Regeneration II				
	Cyclohexane	3010	1.4920	91.0	–
	98-103° fraction of Surakhan gasoline	3750	1.4385	–	36.5
	The same	5925	1.4210	–	29.0
	Cyclohexane	5930	1.4448	32.5	–
	Regeneration III				
	Cyclohexane	5935	1.4915	90.8	–
	98-102° fraction of "Tovarnaya Kalosha" gasoline	6675	1.4559	–	58.0
	The same	7425	1.4431	–	42.0
	The same	8775	1.4230	–	16.0
	Cyclohexane	8780	1.4370	19.7	–
	Regeneration IV				
	Cyclohexane	8785	1.4906	90.0	–
	98-102° fraction of "Tovarnaya Kalosha" gasoline	9525	1.4494	–	51.5
	Cyclohexane	9530	1.4661	62.3	–
	98-102° fraction of "Tovarnaya Kalosha" gasoline	10950	1.4375	–	36.0
	Cyclohexane	10955	1.4475	36.4	–
	Regeneration V				
	Cyclohexane	10960	1.4783	76.8	–
	98-102° fraction of "Tovarnaya Kalosha" gasoline	11700	1.4400	–	42.0
	Cyclohexane	11705	1.4699	66.2	–
	98-102° fraction of "Tovarnaya Kalosha" gasoline	12750	1.4205	–	15.0
	Cyclohexane	12755	1.4594	54.0	–
	Regeneration VI				
	Cyclohexane	12760	1.4740	72.0	–
	98-102° fraction of "Tovarnaya Kalosha" gasoline	13200	1.4363	–	30.0
	Cyclohexane	13205	1.4640	59.7	–

Total: 220 hr. 5 min.

TABLE 3 (Con't)

Catalyst No.	Substance being dehydrogenated	Time from start of work (min.)	Properties of catalyzates		
			n_D^{20}	Conversion of cyclohexane into benzene (%)	toluene content (% by vol.)
8	Cyclohexane	5	1.4975	97.0	–
	98-103° fraction of Surakhan gasoline	75	1.4450	–	43.5
	Unfractionated Surakhan gasoline	2145	1.4405	–	
	Cyclohexane	2150	1.4775	76.0	–
	Unfractionated Surakhan gasoline	8340	1.4350	–	–
	Cyclohexane	8345	1.4578	51.8	–
	Unfractionated Surakhan gasoline	10400	1.4340	–	–
	Cyclohexane	10405	1.4525	44.4	–
	Unfractionated Surakhan gasoline	14965	1.4300	–	–
	Cyclohexane	14970	1.4523	44.2	–
	Total: 249 hr. 30 min.				

EXPERIMENTAL

The investigation of the dehydrogenating activity and stability of the samples of nickel-alumina catalysts that we prepared was carried out under the conditions for the dehydrogenation of cyclohexane and of different samples of the heptane-methylcyclohexane fraction of Maikop straight-run gasoline and of unfractionated Surakhan straight-run gasoline. The narrow gasoline fractions that we isolated had the following properties:

Fraction I, b.p. 98-103°, of Surakhan gasoline had n_D^{20} 1.4152 and d_4^{20} 0.7530, and it contained 3% by volume of toluene.

Fraction II, b.p. 97-103°, of Maikop gasoline had n_D^{20} 1.4170 and d_4^{20} 0.7480; and it contained 12% by volume of toluene.

Fraction III, b.p. 98-102°, of Krasnodar gasoline ("Tovarnaya Kalosha" grade) had n_D^{20} 1.4150 and d_4^{20} 0.7475, and it contained only traces of aromatic hydrocarbons. The unfractionated Surakhan gasoline boiled in the range 72-134°, had n_D^{20} 1.4140 and d_4^{20} 0.7490, and contained about 2% by volume of aromatic hydrocarbons. Unsaturated compounds were absent in all samples (Baeyer's test). The cyclohexane had b.p. 80.8° (760 mm), n_D^{20} 1.4264 and d_4^{20} 0.7780.

Catalysts. Catalysts 4 and 5 were prepared in strict accordance with Zelinskii and Komarevskii's method [7]. Catalysts 6 and 8 were prepared by the coprecipitation of nickelous and aluminum hydroxides from solutions of nickel and aluminum nitrates with sodium hydroxide solution by the following method, as simplified and improved by us.

Method of Preparation of a Nickel-Alumina Catalyst for the Dehydrogenation of Cyclohexanes. A freshly prepared 30% solution of sodium hydroxide was added in the quantity calculated for the formation of nickelous and aluminum hydroxides to a mechanically stirred molar solution of aluminum nitrate. Aluminum hydroxide was formed at first, but then redissolved as aluminate. This solution was stirred vigorously while a molar solution of nickel nitrate in a quantity calculated to be a slight excess was added gradually from a dropping funnel. The precipitation was carried out at room temperature and the operation was stopped when the reaction medium was found to contain an excess of nickel ions (positive reaction with dimethylglyoxime). When the nickel nitrate had been added, stirring was continued for 30 minutes. If no test was then obtained for nickel ions, a solution of a little (2-3 g) of nickel nitrate was added to the suspension of hydroxides. The precipitate was washed by decantation with pure tap water until the diphenylamine reaction for NO_3^- was negative. For the last three washes distilled water was used. The washed catalyst was filtered on a Buchner funnel, formed into wormlike pieces, and dried at 125° to constant weight in a drying oven. In this way we prepared catalyst samples containing 50% Ni (Catalyst 6) and 30% Ni (Catalyst 8).

The proposed method for the preparation of an active dehydrogenation catalyst differs from Zelinskii and Komarevskii's method in the following ways: 1) The irreproducibility of the loss of a large amount of nickel nitrate is eliminated, though a certain excess of nickel ions is ensured on completion of the precipitation of nickelous and aluminum hydroxides. 2) All the alumina (carrier) is taken in the freshly precipitated form. 3) Treatment of the reaction mixture with carbon dioxide is omitted, because it is unnecessary. 4) The solutions of the original salts (nitrates) have a definite concentration (1 M). 5) The bulk of the washing of the catalyst free from NO_3^- ions is carried out with tap water.

Experimental Conditions. The molded and dried catalysts were reduced with electrolytic hydrogen in a glass tube with gradual rise of temperature to 350° [9]. Reduction at this temperature was continued for 16 hours. The dehydrogenation experiments were carried out in the same Pyrex tube of internal diameter 24 mm, which was placed in an electric tube furnace fitted with automatic control. The volume of reduced catalyst was generally 150 ml. The temperature of the tube was maintained at 300 ± 5°. Cyclohexane was introduced from an automatic buret in 5-ml portions, and the gasoline fractions in 75-ml portions at a space velocity of 0.4 $hour^{-1}$ (corresponding to 1 ml per minute) in a weak stream of hydrogen. The catalyzate was collected in an ice-cooled receiver. The activities of the catalysts were checked periodically by passing cyclohexane over them before and after experiments with gasoline fractions and determining the degree of the dehydrogenation of cyclohexane from the refractive index of the catalyzate [13]. The aromatic contents of the catalyzates of the heptane-methylcyclohexane fractions were determined by the sulfuric acid method. The results of determinations of the dehydrogenating activities of the catalysts for cyclohexane are given in Table 1. The durations of the work of the catalysts between regenerations under the conditions of the dehydrogenation of the heptane-methylcyclohexane fractions and also of the unfractionated Surakhan gasoline are shown in Tables 2 and 3 and in Figures 1-3. Regeneration of a spent catalyst in situ was carried out by passage of air at 300° for three hours followed by a six-hour reduction with hydrogen at 300°.

Table 1 shows that Catalysts 6 and 8, prepared by our improved method, had a higher dehydrogenating power than the samples of Zelinskii and Komarevskii's catalyst; they were also more stable (Table 3). The 30% nickel-alumina catalyst was found to be particularly stable, and it was tested not only under the conditions of the dehydrogenation of narrow gasoline fractions, but also on a more complex mixture of hydrocarbons, namely unfractionated Surakhan gasoline. Under these conditions it was found to be capable of carrying out dehydrogenation for 249 hours without regeneration.

Table 2 shows that Catalysts 4 and 5, prepared by Zelinskii and Komarevskii's method, differed in dehydrogenating power and stability. Catalyst 5 was considerably more active and stable than Catalyst 4 for the aromatization of heptane-methylcyclohexane fractions under given conditions. However, after 2245 ml of heptane-methylcyclohexane fraction and 10 ml of cyclohexane had been aromatized over Catalyst 5 the catalyst activity had fallen considerably, as indicated by a fall in the degree of dehydrogenation of cyclohexane into benzene from 90% to 43.4%. After the first regeneration the activity of the catalyst rose almost to its initial level. The degree of dehydrogenation of cyclohexane into benzene was then 89.2%. The amount of the aromatized fraction (97-103°) of Maikop gasoline was 3145 ml. The toluene content of the catalyzates fell gradually from 45% to 28%. However, a second regeneration no longer gave a satisfactory result. The conversion of cyclohexane into benzene in the first check experiment was only 67.0%, and after the aromatization of a further 1600 ml of gasoline fraction this fell to 51.3%. The toluene content of the catalyzate of the gasoline fraction did not then exceed 26.5% by volume. The change in the activity of Catalyst 5 during the aromatization of the 97-103° fraction of Maikop gasoline is shown in Fig. 1.

Table 3 shows that Catalysts 6 and 8, prepared by the improved method, are capable of carrying out the dehydrogenation of heptane-methylcyclohexane fractions and unfractionated Surakhan gasoline (Catalyst 8) in an effective manner over a long period. Catalyst 6 carried out the process for 220 hours, in the course of which it was regenerated six times. By the dehydrogenation of the 98-103° fraction of Surakhan gasoline its toluene content was raised from 2% to 29-42% by volume, and in the catalyzates from the 98-102° fraction of "Tovarnaya Kalosha" gasoline, which contained only traces of toluene, the amount of the latter attained 30-58% by volume. Catalyst 8, which contained 30% of nickel, was found to be capable of carrying out the aromatization even of unfractionated Surakhan gasoline under conditions of continuous working for 249 hours. During the whole period of work it was not regenerated. The combined catalyzate of unfractionated Surakhan gasoline had the following properties: boiling limits 77-144°, n_D^{20} 1.4340, and d_4^{20} 0.7780; it contained 36% by volume of aromatic

hydrocarbons and with 4 ml of R-9 it had an octane rating of 95.2. The octane ratings of the unaromatized gasoline were 75.2 in the pure state and 92.7 with 4 ml of R-9. The quality of the gasoline, as determined by method 3-C, was increased as a result of aromatization from 122 to 160. The changes in the activities of Catalysts 6 and 8 in the aromatization of narrow fractions of Surakhan and Krasnodar ("Tovarnaya Kalosha" grade) gasolines are given in Figures 2 and 3.

SUMMARY

1. As the result of an investigation of the effect of the conditions of the preparation of nickel-alumina catalysts on their dehydrogenating powers, a method is proposed for the preparation of an active, stable, and reproducible catalyst for the dehydrogenation of cyclohexane.

2. The presence of a certain excess of nickel ions in the reaction medium at the end of the precipitation of nickelous and aluminum hydroxides is an essential factor in the preparation of an active form of nickel-alumina dehydrogenation catalyst.

3. Taking the dehydrogenation of cyclohexane, that of heptane-methylcyclohexane fractions of Surakhan and Maikop gasolines, and that of sample of unfractionated Surakhan gasoline as examples, we showed that catalysts prepared by the improved method can be used successfully for the laboratory dehydrogenation both of narrow gasoline fractions and of unfractionated gasolines.

4. A 30% nickel-alumina catalyst prepared by this improved method preserves high activity for a long time (249 hours), without regeneration, in the aromatization of unfractionated Surakhan gasoline.

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SYNTHESIS AND PROPERTIES OF p-DIALKYLBENZENES

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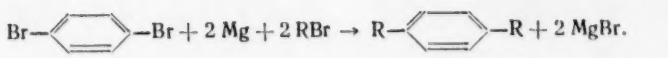
The relation of the surface-active properties and detergency of sodium monoalkylbenzenesulfonates to the length and structure of the alkyl group has been studied fairly thoroughly [1]. The synthesis of alkylbenzenes, in particular dodecylbenzenes, as having the optimum chain length for maximum detergency, has also been described in various papers [2].

The present paper concerns thesynthesis of individual p-dialkylbenzenes with the object of making a further study of the surface-active properties of sodium sulfonates prepared from these compounds. This work is required because of the necessity to determine the extent to which the detergency of dialkylbenzenesulfonates differs from that of monoalkylbenzenesulfonates containing the same number of carbon atoms. This is all the more important in that amylenes, which are obtained as a by-product in the production of cracking gasoline, are already finding use for the alkylation of benzene with the object of obtaining a detergent, namely so-called Azolat, which appears to be a mixture of decyl- and diamyl-benzenesulfonates. There is also another direction in which amylenes can be utilized for the same purpose: they dimerize into decylenes, and alkylation of benzene with these with subsequent sulfonation gives sodium decylbenzenesulfonate (Sulfonol NP-2), which also occurs in admixture with diisoamylbenzenesulfonates because of the ready depolymerizability of diamylenes [3].

The question of the best way to utilize amylenes - for the production of Azolat or the production of Sulfonol NP-2- has not yet been finally settled. This question can be resolved by the determination of the relative amounts of mono- and di-alkylbenzenes in each of these preparations and the comparative evaluation of the surface-active properties and detergencies of mono- and di-alkylbenzenesulfonates. We somewhat extended the range of dialkylbenzenes used in our investigations and dealt with hydrocarbons both with normal and with branched chains. The p-dialkylbenzenes (I)–(VI), the properties of which are presented in Table 1, were synthesized in one stage:



The yields did not exceed 25%.

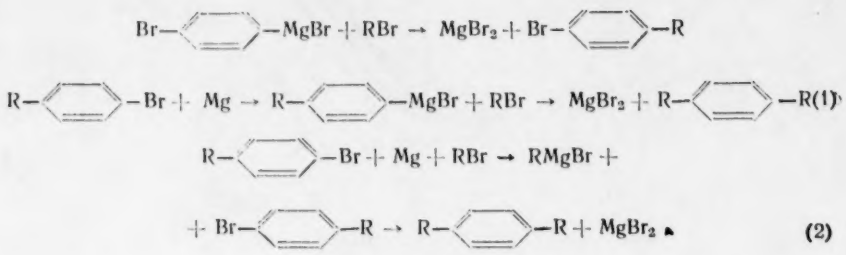
It is known that p-dibromobenzene readily gives a reactive "one-sided" Grignard reagent in ether. It is with this reagent that Grignard syntheses have previously been carried out [4]. Zal'kind and Rogovinskii [5] showed that on long contact of p-dibromobenzene with magnesium the latter was consumed to the extent of 87-88%, this being judged from the amount of hydrogen liberated in the treatment of the residual magnesium with sulfuric acid; however, no direct proofs of the formation of p-phenylenebis [magnesium bromide] were advanced. Lukes and Prelog [6] observed the formation of the product of the reaction of the "two-sided" organomagnesium compound with N-methylsuccinimide. For the synthesis of dialkylbenzenes by the Grignard-Wurtz method, p-dibromobenzene has not been used. In our case, judging from the amount of residual magnesium, a

TABLE 1

Compound	Structure	B.p. in °C (p in mm)	F.p. / m.p. °C	n_D^{20}	d_4^{20}	MR calculated	MR found	Δ MR	Analysis (%) calculated C	calculated H	found C	found H
I	$n\text{-}C_4H_9$–C$_6$H$_4$–$n\text{-}C_4H_9$	98—99 (3)	—94 —30	1,4903	0,8584	63,64	64,14	0,50	88,35	11,65	88,18 88,13	11,71 11,80
II *	$n\text{-}C_5H_{11}$–C$_6$H$_4$–$n\text{-}C_5H_{11}$	91—92 (1)	—63 —49	1,4875	0,8573	72,93	73,32	0,39	88,00	12,00	88,17 87,91	12,00 12,00
III	$n\text{-}C_6H_{13}$–C$_6$H$_4$–$n\text{-}C_6H_{13}$	146—147 (2,5)	—49 —29	1,4862	0,8567	82,23	82,62	0,39	87,72	12,27	87,75 87,60	12,30 12,36
IV	$n\text{-}C_7H_{15}$–C$_6$H$_4$–$n\text{-}C_7H_{15}$	179—180 (4)	—28 —13	1,4858	0,8563	91,53	92,00	0,47	87,52	12,48	87,57 87,71	12,46 12,41
V	$n\text{-}C_8H_{17}$–C$_6$H$_4$–$n\text{-}C_8H_{17}$	180—181 (3)	—9 +3	1,4859	0,8566	100,82	101,28	0,46	87,34	12,66	87,37 87,63	12,43 12,44
VI	$n\text{-}C_9H_{19}$–C$_6$H$_4$–$n\text{-}C_9H_{19}$	210—212 (2)	—12 +7	1,4840	0,8557	110,12	110,52	0,40	87,19	12,81	87,59 87,56	12,57 12,55
VII	$(CH_3)_2CHCH_2CH_2$–C$_6$H$_4$–$CH_2CH_2CH(CH_3)_2$	130—131 (6)	—69 —47	1,4855	0,8509	72,92	73,55	0,63	88,00	12,00	88,16 88,35	11,91 12,00
VIII	$(CH_3)_2CH$–C$_6$H$_4$–$C(CH_3)_2CH_2CH_2CH_3$	88—89 (1,5)	—	1,4927	0,8675	68,39	68,42	0,03	88,16	11,84	88,03 88,17	11,71 11,80
IX	CH_3–C$_6$H$_4$–$C(CH_3)_2-CH_2-(CH_2)_6-CH_3$	144—145 (3)	—	1,4900	0,8656	82,23	82,31	0,08	87,73	12,27	87,27 87,37	12,00 12,10
X	$(CH_3)_2CH$–C$_6$H$_4$–$C(CH_3)_2-CH_2-(CH_2)_3-CH_3$	117—118 (2)	—67 glass	1,4908	0,8626	77,58	78,00	0,42	87,87	12,14	87,32 87,71	11,93 12,10

* This was prepared previously by the acylation method [8]: b.p. 170-175° (20 mm); n_D^{25} 1.4843; d_4^{25} 0.850.

"one-sided" organomagnesium compound was first formed, and on addition of an alkyl bromide to this the 1-alkyl-4-bromobenzene was formed. Reaction of the latter with magnesium gave its organomagnesium compound, which reacted with a second molecule of alkyl bromide with formation of the p-dialkylbenzene, or a Grignard reagent was formed from the alkyl bromide etc.



(2)

TABLE 2

Formula	B.p. in °C (p in mm)	d_4^{20}	n_D^{20}	MR calculated	MR found	ΔMR	Viscosity (centistokes at 20°)
$C_6H_5—C_8H_{17}$-n	131—134 (12)	0,8582	1,4851	63,64	63,57	—0,07	2,93
$C_6H_5—C_{12}H_{25}$-n	183—185 (12)	0,8564	1,4822	82,23	82,06	—0,14	6,294
$C_6H_5—C_{14}H_{29}$-n	153 (0,5)	0,8559	1,4813	91,53	91,31	—0,22	8,97
$C_6H_5—C_{16}H_{35}$-n	171 (0,1)	0,8558	1,4814	100,82	100,67	—0,15	12,29

TABLE 3

Compound	Viscosity (centistokes) 20°	0°	−20°	−40°	Compound	Viscosity (centistokes) 20°	0°	−20°	−40°
I	3,18	4,82	9,75	26,43	V	12,36	26,89	—	—
II	4,67	8,19	20,69	80,82	VI	17,77	90,93	—	—
III	6,51	12,50	35,29	150,30	VII	5,05	9,36	24,82	91,63
IV	9,23	19,20	59,64	—					

When we separated unchanged magnesium from the Grignard reagent and then added the alkyl bromide, the p-dialkylbenzene could not be obtained, which indicates initial formation of the monomagnesium derivative, but does not enable us to choose between Schemes (1) and (2). Pure p-dialkylbenzenes were isolated from the reaction mixture by repeated fractional distillation. Diisopentylbenzene (VII) was prepared by the Friedel-Crafts reaction by the acylation of isopentylbenzene prepared from isobutylmagnesium chloride and benzaldehyde with isovaleryl chloride and subsequent reduction of the ketone. Compounds (VIII)—(X) (Table 1) were prepared by the chloroalkylation of toluene and cumene with 2-methylallyl chloride [7], condensation of organomagnesium compounds prepared from the products with aldehydes, dehydration of the alcohols formed, and hydrogenation of the alkenylbenzenes. These compounds contained only 80-90% of p-isomer.

Schmidt and co-workers [9], with the object of studying the effect of the length of the alkyl group in alkylbenzenes on density, refractive index, and viscosity, synthesized a series of monoalkylbenzenes; the properties of some of these are presented in Table 2. We considered it to be of interest to compare these properties with those of p-dialkylbenzenes containing the same numbers of carbon atoms. It was found that the densities (d_4^{20}) of p-dialkylbenzenes were only about 0.0004 and the refractive indices (n_D^{20}) about 0.0045 (average value) greater than for the corresponding monoalkylbenzenes. The average value of the exaltation of molecular refraction (ΔMRd) for p-dialkylbenzenes, calculated from Vogel's data [10] (Table 1), was + 0.43; when account

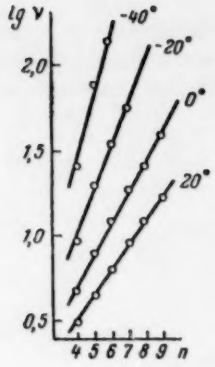


Fig. 1

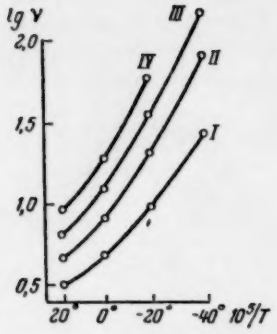


Fig. 2

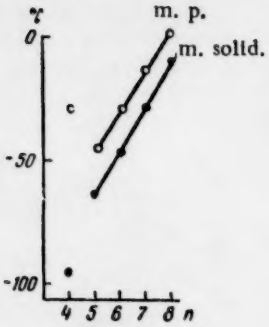


Fig. 3

was taken of the type of bonds by Tatevskii's method [11], the value was + 0.17; for monoalkylbenzene the respective values were −0.15 and 0.10 (Table 2). Worse results were obtained in the calculation of molecular volumes [11]; in this case the difference between found and calculated values was about + 3 ml/mole.

Kinematic viscosities at + 20.0°, 0°, −20°, and −40° were determined for the p-dialkylbenzenes (I)–(VII) (Table 3).

In the temperature range studied by us, with increase in the length of the alkyl group in the compounds (I)–(VI) the logarithm of the viscosity rises linearly (Fig. 1). For 20° and 0° this linear relation may be expressed by the equations:

$$\log \nu_{+20^\circ} = 0.142 \cdot n - 0.04;$$

$$\log \nu_{0^\circ} = 0.19 \cdot n - 0.04.$$

As the number of measurements was insufficient, we could not write similar equations for −20° and −40°. Fig. 2 gives a graphical representation of the changes of the viscosities of the compounds (I)–(IV) in the temperature range from −40° to +20°. The viscosities of monoalkylbenzenes at 20° are less than those of the p-dialkylbenzenes having corresponding numbers of carbon atoms by 0.24 centistoke on the average. Compounds (I)–(VII) freeze to form crystals, whose melting points were determined. With increase in the length of the alkyl groups the melting point (t_m) rises linearly in the series of compounds (II)–(V) (Fig. 3) and may be described by the equation:

$$t_m = 16 \cdot n - 125.$$

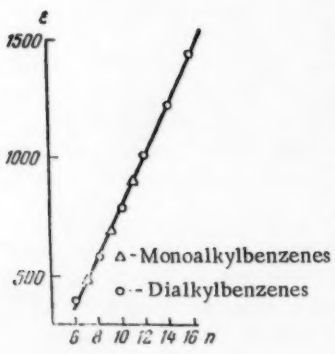


Fig. 4

With dialkylbenzenes, as with monoalkylbenzenes, there is an appreciable difference between melting point and freezing point, and this diminishes with increase in the length of the group. Freezing point also rises linearly from dipentyl- to dioctyl-benzene (Fig. 3). Comparison of the melting points of n-alkylbenzenes given in the literature with those of the p-dialkylbenzenes (I)–(VI) that we synthesized enables us to conclude that the melting points of the latter are 20-25° lower than those of the n-alkylbenzenes of the same molecular weight. For example, the melting point of dodecylbenzene is 7° [12], and that of p-dihexylbenzene is −29°; the melting point of octadecylbenzene is 33° [13], and that of p-dinonylbenzene is 7°. For the p-dialkylbenzenes (I)–(V) infrared spectra were determined in the range 2-15 μ on an IKS-11 spectrometer with NaCl and LiF prisms Analysis of the spectra enabled us to establish that with increase in the number of methylene groups (n') in the molecule the extinction coefficient (ε) of the 2930 cm^{-1} band

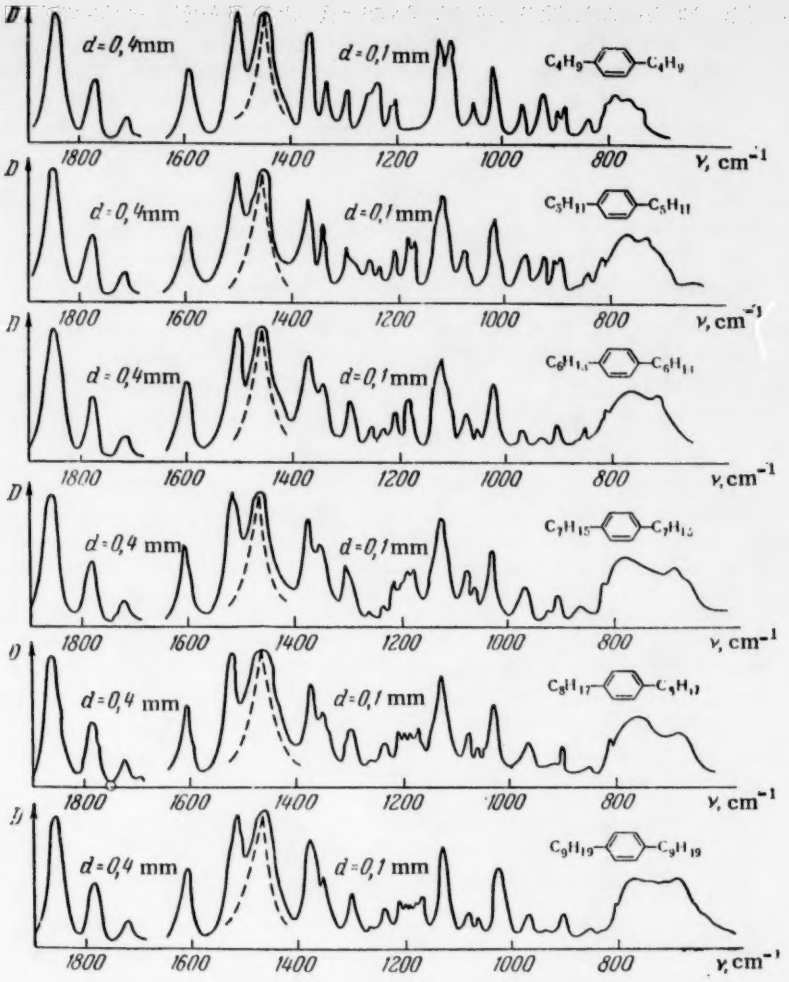


Fig. 5

rises linearly. A similar linear relation is observed in the infrared spectra of octyl-, decyl-, and dodecyl-benzenes, which we prepared specially for this purpose from phenyllithium and the corresponding alkyl bromides. The relation of the extinction coefficient to the number of CH_2 groups ($\epsilon = 106 \cdot n' - 250$) holds very closely (within about 2%). The graph obtained from the average values of numerous measurements (Fig. 4) therefore enables us to determine the numbers of CH_2 groups in the alkyl groups of alkylbenzenes. The infrared spectra of compounds (I)–(VI) are given in Fig. 5*.

EXPERIMENTAL

p-Dialkylbenzenes (I)–(IV). We shall describe the synthesis of p-dihexylbenzene; the other p-dialkylbenzenes were prepared in an analogous way. A solution of 240 g (1 mole) of p-dibromobenzene in ether was added over a period of 3.5 hours to 57.62 g (2.4 moles) of magnesium in 500 ml of ether; the reaction mixture was stirred for 90 minutes at the boiling point of ether, and over a period of 2.5 hours 413 g (2.5 moles) of hexyl bromide was added. The reaction mixture stood overnight, ether was distilled off, and the residual thick mass

* The infrared spectra and the relation of ϵ to n' were determined by V. Shlyapochnikov, to whom we express our thanks.

was heated at 110° for one hour; part of the unchanged hexyl bromide was then distilled off, and heating was continued for ten hours at 160°. The reaction mixture was then cooled, the ether that had been distilled off was returned to the flask, and its contents were decomposed with water and dilute hydrochloric acid. By repeated fractional distillation over sodium, 49 g (23%) of p-dihexylbenzene was isolated from the ethereal solution. The remaining syntheses were also carried out at 140-160° with prolonged (10-20 hours) heating of the reaction mixture.

p-Diisopentylbenzene (VII). a) Benzaldehyde (212 g, 2 moles) was added to a Grignard reagent prepared from 184 g (2 moles) of isobutyl chloride and 60 g (2.5 moles) of magnesium. From the resulting α-isobutylbenzyl alcohol (280 g, 85%), dehydration over $KHSO_4$ and subsequent hydrogenation over Raney nickel in an autoclave gave isopentylbenzene, b.p. 93-96° (35 mm) and n_D^{20} 1.4889.

b) Aluminum chloride (200 g, 1.5 moles) was added at 0-5° over a period of several hours in portions to a mixture of 145 g (1 mole) of isopentylbenzene, 180 g (1.5 moles) of isovaleryl chloride, and 200 ml of nitrobenzene. The reaction mixture was left overnight and then treated in the usual way. We obtained 211 g (91%) of 4' -isopentylisovalerophenone; b.p. 149-150° (3 mm); n_D^{20} 1.5049; d_4^{20} 0.9233; found MR 74.63; calculated MR 77.90.

c) 4' -Isopentylisovalerophenone (200 g, 0.82 mole) and hydrochloric acid (600 ml) were added to 600 g of granulated zinc amalgamated with a hydrochloric acid solution of mercuric acetate. The mixture was stirred and boiled for 60 hours; in the course of time a further 700 ml of hydrochloric acid was added. Distillation of the organic layer gave 150 g (85%) of p-diisopentylbenzene.

2-p-Cumenyl-2-methylpentane (VIII). By the previously described method [2], from 147.5 g (0.7 mole) of p-[1-(chloromethyl)-1-methylethyl] cumene, 29.2 g (1.2 moles) of magnesium, and 100 g (2.17 moles) of acetaldehyde we prepared 109 g (70%) of 4-p-cumenyl-4-methyl-2-pentanol; b.p. 108-110° (2 mm); d_4^{20} 0.9440; n_D^{20} 1.5030. The alcohol was dehydrated by distillation over $KHSO_4$, and the resulting alkenylcumene was hydrogenated in an autoclave over Raney nickel at 120-130 atm and 50°; the product was distilled over sodium. The absence of unsaturated compounds in the hydrocarbon obtained was checked from the bromine value and an analysis of the infrared spectrum.

2-p-Cumenyl-2-methylheptane (X). In a similar way, from p-[1-(chloromethyl)-1-methylethyl] cumene and butyraldehyde we prepared 2-p-cumenyl-2-methyl-4-heptanol; b.p. 139-141° (3 mm); d_4^{20} 0.9252; n_D^{20} 1.5000; yield 70%. The alcohol was converted as before into the corresponding hydrocarbon.

2-Methyl-2-p-tolyldecane (IX). Reaction of a Grignard reagent prepared from 200 g (1.1 moles) of p-[1-(chloromethyl)-1-methylethyl] toluene and 36.5 g (1.5 moles) of magnesium with 137 g (1.2 moles) of heptanol gave 187 g (71%) of 2-methyl-2-p-tolyl-4-decanol; b.p. 132-133° (2 mm); d_4^{20} 0.9230; n_D^{20} 0.4992. The alcohol was dehydrated by boiling it with 60% sulfuric acid (1.5 times the weight of alcohol). The alkenyltoluene was hydrogenated in an autoclave over Raney nickel at 120 atm and 40°.

SUMMARY

1. A series of p-di-n-alkylbenzenes was prepared for the first time by organomagnesium synthesis from p-dibromobenzene, and their viscosity properties and freezing points were studied.

2. By a two-stage synthesis (chloroalkylation of alkylbenzenes and Grignard condensation of the products with aldehydes) dialkylbenzenes containing branched chains were prepared.

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SYNTHESIS OF SULFUR-CONTAINING SUBSTANCES FROM VINYL ETHERS AND ACETYLENE

COMMUNICATION 23. OXIDATION OF VINYL SULFIDES AND SOME PROPERTIES OF VINYL SULFOXIDES AND SULFONES

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The oxidation of organic sulfides is at present attracting much attention from investigators, particularly in connection with the study of the nature of the autoxidative processes occurring in the aging of vulcanized rubber [1, 2]. It was shown that, both in autoxidation and in oxidation with alkyl hydroperoxides, very often not only simple oxidation products (sulfoxides) are formed [1], but also complex decomposition products [2]. The latter include, in particular, unsaturated sulfides of the allyl type and cyclic sulfides with a vinyl double bond [2].

We were interested in the optimum conditions for the oxidation of vinyl sulfides to vinyl sulfoxides and sulfones, i.e., oxidation with preservation of the double bond. Kohler and Potter [3] showed that oxidation of the stereoisomeric styryl tolyl sulfides with hydrogen peroxide in glacial acetic acid at low temperature gives an almost quantitative yield of a mixture of stereoisomeric sulfoxides or sulfones. Kochetkov and Vinogradova [4] have recently used similar conditions for the oxidation of the 2-acylvinyl aryl sulfides (RCOCH=CHSAr) which they synthesized. The yields of sulfoxides were 25-60%, and the yields of sulfones were 30-40% for R = = alkyl and 96% for R = aryl.

However, for unsubstituted vinyl sulfides of the aliphatic series the optimum conditions of oxidation have apparently not been found. Thus, Price and Gillis [5] obtained 17% of methyl vinyl sulfoxide by the oxidation of methyl vinyl sulfide with sodium hypochlorite; from the same sulfide the sulfone was obtained in only 16% yield by oxidation with hydrogen peroxide in glacial acetic acid [5]. Hence, further investigations have not confirmed earlier claims in a German patent [6] for a method of preparation of vinyl sulfoxides and sulfones in good yield from various vinyl sulfides by the action of such oxidizing agents as hydrogen peroxide, sodium hypochlorite, etc. The object of the present work was the determination of the conditions for the selective oxidation of sulfur in vinyl sulfides, mainly of the aliphatic series, and the study of some properties of vinyl sulfoxides and sulfones.

We showed that, for the preparation of vinyl sulfoxides in good yield (60-70%) and as the only reaction product, it is best to carry out the oxidation in an acetone** medium with an equimolecular amount of 70-80% hydrogen peroxide:

$$CH_2{=}CHSR \xrightarrow[-5{+}20^\circ;\ 48{-}50\ \text{hrs.}]{H_2O_2} CH_2{=}CHSOR .$$

* Deceased

** In methanol the yield of sulfoxide is somewhat lower.

TABLE 1

Vinyl Sulfoxides $CH_2 = CHSOR$

R	B.p. in °C (p in mm)	n_D^{20}	$[d_4^{20}$	Unoxidized sulfide (%)	Yield(% on sulfide taken)	
					sulfoxide	sulfone
CH_3*	58,5—59°(6)	1,4951	1,0876	not determined	70	—
C_2H_5	54,5(2)	1,4900	1,0422	10—2	60—75	—
C_3H_7	83(8)	1,4870	1,0125	8	60—70	—
C_4H_9	80—83(2)	1,4830	0,9891	20	65—75	—
$C_4H_9OCH_2CH_2$	113—114(2)	1,4765	1,0138	20	44—58	—
C_6H_5**	104—106(2)	1,5869	1,1629	—	58—74	4—5

* The literature [5] gives b.p. 46-47° (0.8 mm).

** The literature [8] gives b.p. 93-95° (0.2 mm). The other vinyl sulfoxides are not described in the literature.

Despite the long duration of the experiment, part of the sulfide remains unoxidized. This indicates that the sulfur atom in vinyl sulfides is substantially less reactive than that in saturated sulfides [7] evidently because of reduction in the accessibility of the electrons of sulfur due to conjugation of the type

$$CH_2=CH-\ddot{S}R.$$

If 27-30% peroxide is used in the oxidation, as earlier recommended in the patent [6], the yield of sulfoxide does not exceed 50-55%. Oxidation with 30% peroxide in formic acid leads to a complex mixture of oxidation and addition products.

The lower alkyl vinyl sulfoxides are mobile liquids, readily soluble in water and most organic solvents, distillable in a vacuum without decomposition*, and stable to keeping in a sealed tube for a long time without darkening. The properties of the vinyl sulfoxides are given in Table 1.

For the preparation of vinyl sulfones it was earlier recommended [6] that vinyl sulfides be heated with excess of 30% hydrogen peroxide in presence of pyridine. We showed that only aryl vinyl sulfones could be prepared in this way in good yield. In the oxidation of alkyl vinyl sulfides, rise in reaction temperature leads to the formation of a mixture of vinyl sulfoxides, vinyl sulfones, and particularly water-soluble substances of a polymeric character.

Vinyl sulfones may be obtained by the oxidation of vinyl sulfides with peroxybenzoic acid (Prilezhaev's reagent**) or peroxyacetic acid (Table 2):

$$CH_2=CHSR \xrightarrow[2CH_3COOH]{2C_6H_5COOOH} CH_2=CHSOR \longrightarrow CH_2=CHSO_2R.$$

* Alkyl vinyl sulfoxides do not stand overheating and were therefore fractionated from a small flask with a short column. When an attempt was made at fractionation at 5-7 mm through an all-glass column (height of working part 40 cm), ethyl vinyl and, particularly, butyl vinyl sulfoxides partly decomposed.

** Lewin [9] used this reagent for the oxidation of divinyl sulfide to the sulfoxide and sulfone and also for the quantitative titration of sulfide sulfur.

TABLE 2

Vinyl Sulfones $CH_2 = CHSO_2R$

R	B.p. in °C (p in mm)	n_D^{20}	d_4^{20}	Yield in different methods		
				30% H_2O_2	H_2O_2 + SeO_2	Peroxy acid
C_2H_5*	87—88(2)	1,4643	1,1497	21,2	71	75 (CH_3OOOH) 66 (C_6H_5COOOH)
C_3H_7	98—100(3)	1,4642	1,1060	—	66	—
C_4H_9**	116—117(5)	1,4630	1,0776	39,7	55—60	—
C_6H_5***	m.p. 67,5—68	—	—	55,3	—	—

* The literature gives: b.p. 107° (9 mm); n_D^{21} 1.4622 [12]; b.p. 106-108° (8 mm) [13]; b.p. 84-85° (1 mm) [14].

** The literature [15] gives b.p. 135° (15 mm).

*** The literature gives: m.p. 68.5° [16]; m.p. 72° [12]; m.p. 67.5-68.5° [17].

TABLE 3

Molecular Refractions of Vinyl Sulfides, Sulfoxides, and Sulfones*

R	CH_2=CHSR		CH_2=CHSOR		CH_2CHSO_2R	
	MR		*MR*		*MR*	
	found	calculated	found	calculated	found	calculated
CH_3			24,16	24,059	—	—
C_2H_5	28,37	28,04	28,88	28,67	28,88	28,64
C_3H_7	32,89	32,78	33,52	33,41	33,44	33,38
C_4H_9	37,47	37,40	38,17	38,03	37,83	37,99
$C_4H_9OCH_2CH_2$	48,50	48,28	49,06	48,91	—	—
C_6H_5	44,05	43,60	43,44	43,67	—	—

* In the calculation the following values of atom and group refractions were used: S in dialkyl sulfides 7.96 and in alkyl aryl sulfides 8.52 [25]; >SO 8.59 and $>SO_2$ 8.56 [26].

The double bond remains intact, which is indicated by the absence of residues of polymer. The vinyl sulfones obtained in this way contain small amounts of unoxidized sulfoxides as impurity, and it is difficult to purify them from these. Hence, for preparative purpose it is much more convenient to oxidize the sulfide to sulfone with excess of concentrated hydrogen peroxide in t-butyl alcohol in presence of selenium dioxide (at least 5 g per mole of H_2O_2). By this method we were able to prepare vinyl sulfones not containing sulfoxides as impurity (Fig. 1). In this case the oxidizing agent appears to be selenic acid, as earlier suggested by Smith and Holm [10], who proposed oxidation with hydrogen peroxide in presence of SeO_2 as a method for the preparation of acrylic and methacrylic acids from the corresponding aldehydes. Under comparable conditions, hydrogen peroxide in t-butyl alcohol, but without SeO_2, and also t-butyl hydroperoxide oxidize vinyl sulfides only to sulfoxides. No side reactions were observed in oxidation in presence of SeO_2, though for other unsaturated compounds this compound is a fairly good catalyst for the hydroxylation of double bonds with H_2O_2 [11].

In recent literature [5, 17-23] there has been a renewal of interest in the question of the nature of the S—O bond in sulfoxides and sulfones, is it a true double bond with participation of the d shell of sulfur or a singly covalent semipolar bond with preservation of the octet around the sulfur atom? From our point of view

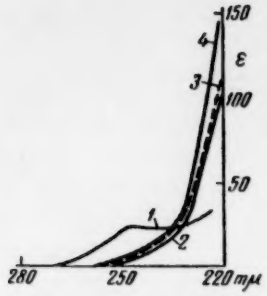

Fig. 1. Ultraviolet absorption spectra of vinyl sulfones: 1) ethyl vinyl sulfone prepared by oxidation with BzOOOH; 2) ethyl vinyl sulfone prepared by oxidation with H_2O_2 + +SeO_2; 3) proply vinyl sulfone prepared likewise; 4) butyl vinyl sulfone prepared likewise.

the posing of the question in such a categorical form is not altogether correct, because in the real molecule the bond probably has an intermediate character with partial participation of the d shell. In any case, proofs that the bond has this or the other nature, as given in previous papers, are not very convincing. Thus, as one of the proofs of the semipolar nature of this bond is given the fact that the molecular refraction rises by a very small amount as we pass from sulfides to the corresponding sulfoxides and sulfones [5, 25]. The same regularity is observed in the series of compounds that we synthesized (Table 3). However, this can be explained with equal success by the properties of S–O bonds formed with participation of the d electrons of the S atom.

Moreover, Price and co-workers consider [5, 17, 22, 23] that the character of the ultraviolet and infrared spectra of some vinyl sulfones and sulfoxides also favors the view that the S–O bond is semipolar because these authors did not detect any clear signs of the conjugation of C = C and S = O groupings in these spectra. For the substances synthesized we determined the ultraviolet absorption spectra and also the intensities of some characteristic lines in the Raman spectra (Table 4).

These results show that there are indications in the spectra that conjugation exists in vinyl sulfoxide and sulfone molecules. Thus, the C = C frequencies in the Raman spectra are appreciably lower than those of olefins, though there is no appreciable increase in intensity. For S–O bonds there is no lowering of frequency as compared with the saturated sulfoxide or sulfone, but the intensity is greatly different, being lower in the unsaturated compounds. Hence, there is undoubtedly some interaction of S–O groups with double bonds, but these data are inadequate for the purpose of determining the nature of the S–O bond. As regards the ultraviolet spectra, we found that in heptane all the vinyl sulfoxides have a fairly intense maximum at 247 mμ which is substantially displaced from the maximum of saturated sulfoxides and permits the detection of even small amounts of vinyl sulfoxide impurity in vinyl sulfones. This will be seen from Fig. 1, in which Curve 1 refers to a sample of ethyl vinyl sulfide containing 1-2% of sulfoxide impurity and obtained by the oxidation of the sulfide with peroxybenzoic acid. Vinyl sulfones prepared by oxidation in presence of SeO_2 (Curves 2-4) did not contain such impurities. When the ultraviolet spectra of vinyl sulfoxides were determined in alcohol, there was a considerably less intense maximum at about 230 mμ, probably because of interaction with the solvent (Fig. 2). This led Price and Gilbert [22] into error: they used the ultraviolet spectrum of methyl vinyl sulfide as evidence of weak conjugation in this molecule and therefore of the purely semipolar nature of the S–O bond, which probably does not correspond with reality.

In conclusion we may point out that in this paper we give methods for the synthesis of alkyl vinyl sulfoxides and sulfones from vinyl sulfides, which are readily synthesized by the vinylation of thiols [24]. They may therefore successfully compete with other previously described methods of synthesis, which are multistage processes based on the use of such toxic compounds as mustard gas derivatives [12, 15, 17, 23].

$$\underset{\diagdown O \diagup}{CH_2{-}CH_2} + RSH \longrightarrow HOCH_2CH_2SR \xrightarrow{H_2O_2} HOCH_2CH_2\underset{(SO_2)}{SOR} \longrightarrow$$

$$\xrightarrow{HCl} ClCH_2CH_2\underset{(SO_2)}{SOR} \xrightarrow{-HCl} CH_2{=}CH\underset{(SO_2)}{SOR}.$$

EXPERIMENTAL

All the vinyl sulfides were prepared by the vinylation of the corresponding thiols [24]. Peroxybenzoic acid was prepared by an improved modification [29] of Prilezhaev's method [28]. Concentrated hydrogen peroxide and peroxyacetic acid were prepared as described by Arbuzov [30].

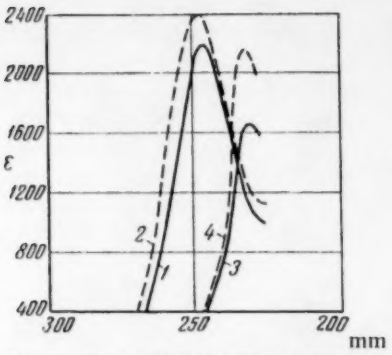

Fig. 2. Ultraviolet absorption spectra: of $CH_2 = CH-SO-CH_3$ 1) in heptane and 3) in alcohol; of $CH_2=CH-SO-C_2H_5$ 2) in heptane and 4) in alcohol.

The ultraviolet spectra were measured in heptane or alcohol solution with the aid of an SF-4 spectrophotometer (limit of measurement 220 mμ). Raman spectra were determined with the aid of an NSP-51 spectrograph. The positions of the lines were determined on the pure liquids, but the intensities were determined in carbon tetrachloride solution. The unit of intensity was taken as one-hundredth of the integral intensity of the lines at 313 cm^{-1} of carbon tetrachloride, the spectrum being excited by the mercury line at 4358 A.

Vinyl Sulfoxides

Ethyl Vinyl Sulfoxide. A 70% solution of hydrogen peroxide (2.7 ml, 0.105 mole) was added dropwise to a stirred mixture of 8.8 g (0.1 mole) of ethyl vinyl sulfide and 8 ml of acetone (cooled with snow and salt) at such a rate that the temperature of the reaction mixture did not exceed 5°. The mixture was stirred for ten hours at 0-5°, left for 35-40 hours at room temperature, and then heated for three hours in a water bath at 60-70° (after a preliminary addition of anhydrous Na_2SO_4). A qualitative test showed the absence of H_2O_2 *. Acetone and unoxidized vinyl sulfide were vacuum-evaporated (trap surrounded by acetone and solid carbon dioxide). Distillation of the residue gave 8.0 g (77.4%) of ethyl vinyl sulfoxide; b.p. 75-76° (4 mm); n_D^{20} 1.4920. After repeated fractionation the residue had: b.p. 54.2° (2 mm); n_D^{20} 1.4900; d_4^{20} 1.0422. Found: C 45.70; 45.70; H 7.87; 7.66; S 30.43; 30.67%. C_4H_8OS. Calculated: C 46.10; H 7.70; S 30.73%. By titration of the contents of the trap by the mercuric chloride method [31], 2.1 g (about 22%) of unchanged ethyl vinyl sulfide was found.

Propyl Vinyl Sulfoxide. This was prepared by the same method, but without heating toward the end of the experiment, from 10.2 g (0.1 mole) of propyl vinyl sulfide and 0.14 mole of H_2O_2 in the form of a 70% solution in 13 ml of acetone; yield 8.2 g (69.5%); b.p. 83° (8 mm); n_D^{20} 1.4870; d_4^{20} 1.0125. Found: C 50.57; H 8.74; 8.72; S 26.70; 26.72%. $C_5H_{10}SO$. Calculated: C 50.85; H 8.54; S 27.11%.

Butyl Vinyl Sulfoxide. This was prepared by the same method from 58 g (0.5 mole) of butyl vinyl sulfide and 0.55 mole of H_2O_2 as a 70% solution in 40 ml of acetone; yield 43 g (65.1%); b.p. 88-90° (6 mm); n_D^{20} 1.4840; d_4^{20} 0.9891. Found: C 54.26; 54.26; H 8.77; 8.87; S 24.12; 24.32%. $C_6H_{12}SO$. Calculated: C 54.54; H 9.16; S 24.27%.

2-Butoxyethyl Vinyl Sulfoxide. This was prepared by the same method from 8.6 g (0.053 mole) of 2-butoxyethyl vinyl sulfide and 0.055 mole of H_2O_2 as a 78% solution in 9 ml of acetone; yield 6.0 g (58.2% b.p. 113-114 (2 mm); n_D^{20} 1.4765; d_4^{20} 1.0138. Found: C 54.43; 54.23; H 9.28; 9.44; S 18.24; 18.24%). $C_8H_{16}SO_2$. Calculated: C 54.54; H 9.09; S 18.1%.

Methyl Vinyl Sulfoxide. By the same method, from 11 g (0.149 mole) of methyl vinyl sulfide (prepared in 32.3% yield by the vinylation of methanethiol) and 4.29 ml (0.163 mole) of 78% H_2O_2 solution in 11 g of acetone we obtained 8.5 g of methyl vinyl sulfoxide; b.p. 49-50.5° (4 mm); n_D^{20} 1.4948. After repeated fractionations: b.p. 58.5-59° (6 mm); n_D^{20} 1.4951; d_4^{20} 1.0876. Found: C 39.87; 6.71%. C_3H_6SO. Calculated: C 39.95; H 6.712%.

Phenyl Vinyl Sulfoxide. By the same method, from 14 g (0.103 mole) of phenyl vinyl sulfide and 3.8 g (0.11 mole) of H_2O_2 (as a 57% solution) in 25 ml of acetone we obtained 11.5 g (73.7%) of phenyl vinyl sulfoxide; b.p. 104-106° (2 mm); n_D^{20} 1.5774; after repeated fractionation: b.p. 132-133° (7 mm); n_D^{20} 1. 5869; d_4^{20} 1.1629. Found: C 62.97; 62.74; H 5.42; 5.54; S 21.01; 21.00%. C_8H_8SO. Calculated: C 63.14; H 5.30; S 21.07%.

From a series of experiments we obtained also small amounts of higher-boiling fractions (b.p. 126-128°) (3.5-4%), which later crystallized out and were found to be contaminated phenyl vinyl sulfone (m.p. after recrystallization, 66.5-67°).

* An attempt to vacuum-evaporate solvent 24 hours after the start of the oxidation in one of the experiments on the synthesis of phenyl vinyl sulfoxide led to an explosion. Further experiments were prolonged for not less than 44-48 hours, and if unconsumed peroxide was present it was decomposed by the addition of MnO_2.

TABLE 4

Spectra of Vinyl Sulfoxides and Sulfones

Substance	$-\omega(cm^{-1})$		I		λ_{max}	
	C=C	S–O	C=C	S–O	mμ	ε_{max}
$CH_2=CHSOCH_3$	—	—	—	—	245	2300
$CH_2=CHSOC_2H_5$	1601	1060 1032	26	25	247	2400
$CH_2=CHSOC_3H_7$	1601	1070 1030	28	25	247	2600
$CH_2=CHSOC_4H_9$	1602	1060 1030	30	25	247	2600
$C_2H_5SOC_2H_5$*	—	1068 1025	—	—	222**	1300
$CH_2=CHSO_2C_2H_5$	1615	1126	32	48	220**	120
$CH_2=CHSO_2C_3H_7$	1616	1128	26	38	220**	150
$CH_2=CHSO_2C_4H_9$	1615	1128	30	40	220**	110
$C_2H_5SO_2C_2H_5$*	* —	1136	—	~100***	—	—
$CH_2=CHR$	1642	—	30	—	—	—

*Diethyl sulfoxide and sulfone were prepared by the oxidation of diethyl sulfide with hydrogen peroxide in acetone and their physical properties were in accord with data in the literature. The ultraviolet spectra of the sulfoxides were determined in heptane solution, and those of the sulfones were determined in ethanol solution.

**For these compounds the absorption coefficients given in the table are for the region of 220 mμ; the maxima probably lie at shorter wavelengths.

***From data in [27].

TABLE 5

Oxidation of Ethyl Vinyl Sulfide with 28-30% H_2O_2 at 80°

Duration of heating (hr.)	Ethyl vinyl sulfoxide (%)	Ethyl vinyl sulfone (%)	Polymeric residue (% on weight)
1	38,5	—	22
2	45	10	28
10	10—12	21,2	57
60	—	—	80—90

TABLE 6

Oxidation of Ethyl Vinyl Sulfide (EVS) with H_2O_2 in t-Butyl Alcohol (40 ml)

Amount taken of			Reaction conditions		Yield of reaction products (%)	
EVS (moles)	H_2O_2 (moles)	SeO_2 (g)	total duration (hr.)	temp. in °C (time in hr.)	vinyl sulfoxide	vinyl sulfone
0,1	0,22	1,0	48	60—70(4)	—	71
0,1	0,22	0,5	48	60—70(4)	35	50
0,1	0,22	—	72	60—70(4)	60	10

Oxidation with H_2O_2 with Heating. a) Pyridine (0.44 ml) was added to 8.8 g (0.1 mole) of ethyl vinyl sulfide, and the mixture was stirred while 28.5 ml of 28% hydrogen peroxide (0.23 mole of H_2O_2) was added dropwise. On the addition of H_2O_2 the temperature remained in the range 20-40° and was then raised to 80°. The stirred reaction mixture was heated at this temperature for ten hours. First the homogenization of the reaction mixture was observed, and then an oily layer was precipitated on the bottom of the flask. The excess of H_2O_2 was decomposed by addition of MnO_2, and water was vacuum-distilled off. The residue was diluted with chloroform and dried with sodium sulfate; chloroform was distilled off, after which we isolated 1.2 g of ethyl vinyl sulfoxide admixed with some sulfone [b.p. 62-79° (3 mm); n_D^{20} 1.4760] and 2.55 g (21.2%) of ethyl vinyl sulfone; b.p. 89-93° (3 mm); n_D^{20} 1.4628; d_4^{20} 1.1407. Found: C 40.33; 40.20; H 6.75; 6.74; S 26.76; 26.95%. $C_4H_8SO_2$. Calculated: C 40.00; H 6.60; S 26.60%.

The residue (5 g) was an undistillable resin, which was the only product in experiments with more prolonged heating. For the preparation of this polymeric substance in a purer form, in another experiment the low-boiling fractions were distilled off at $2 \cdot 10^{-2}$ mm. The residue was dried to constant weight in the same vacuum. Found: C 40.80; 40.90; H 6.99; 6.92; S 21.81; S 21.74%. $(C_4H_8SO_2)n$. Calculated: C 40.00; H 6.60; S 26.60%. In analysis the residue did not correspond to the polymer of the vinyl sulfone. The residue was soluble in dioxane and water, less soluble in chloroform, and almost insoluble in carbon tetrachloride. In solubility and appearance it corresponded to the product erroneously regarded by Reppe [6] as ethyl vinyl sulfone. The yields of sulfoxide, sulfone, and polymeric residue obtained under other conditions are given in Table 5.

b) When 4 g (0.035 mole) of butyl vinyl sulfide was heated with 9.3 g (0.07 mole of H_2O_2) of 27% hydrogen peroxide in presence of 0.4 ml of pyridine, we obtained 0.5 g of a mixture of butyl vinyl sulfoxide and sulfone (b.p. 93-100° (1 mm) and n_D^{20} 1.4712) and 2.03 g (39.8%) of butyl vinyl sulfone; b.p. 103-106° (3 mm); n_D^{20} 1.4640; d_4^{20} 1.0657. Found: C 48.86; 48.88; H 8.34; 8.43; S 21.67; 21.78%. $C_6H_{12}SO_2$. Calculated: C 48.58; H 8.20; S 21.63%. The polymeric residue, which was not investigated further, amounted to 2.0 g (50% on the weight of sulfide taken).

c) When 8.4 g (0.06 mole) of phenyl vinyl sulfide was oxidized for 60 hours with 15.7 g (0.23 mole) of hydrogen peroxide in the form of a 31% solution in presence of 0.26 ml of pyridine, we obtained 5.7 g (55.3%) of phenyl vinyl sulfone, m.p. 67.5-68° after two crystallizations from a mixture of benzene and petroleum ether.

Oxidation with Peroxy Acids. a) At −10° a solution of 0.12 mole of peroxybenzoic acid in 250 ml of chloroform was added to a solution of 5.2 g (0.058 mole) of ethyl vinyl sulfide in 50 ml of chloroform. The mixture was stirred at this temperature for four hours, and was then left at room temperature until a qualitative test for peroxide was negative (40 hours). Benzoic acid was neutralized by passage of a stream of dry ammonia at −10°, ammonium benzoate was filtered off, and solvent was vacuum-evaporated. Distillation of the residue gave 4.7 g (66%) of ethyl vinyl sulfone, b.p. 78-79° (1 mm) and n_D^{20} 1.4620. According to the ultraviolet spectrum (Fig. 1) the sulfone contained 1-2% of vinyl sulfoxide impurity.

b) A solution of 4.4 g (0.05 mole) of ethyl vinyl sulfide in 30 ml of ether was cooled to −20°, and 12.5 g (0.11 mole) of 67% peroxyacetic acid was added (the temperature was kept between −10° and 0°). The reaction mixture was stirred for 30 minutes with cooling and two hours at room temperature, after which the acetic acid was neutralized by the addition of 16.6 g of anhydrous potassium carbonate. After 40 hours the mixture was filtered off from the precipitate, which was washed repeatedly with ether; solvent was vacuum-evaporated, and we then obtained 1.2 g (10%) of a mixture of ethyl vinyl sulfoxide and sulfone, b.p. 65-86° (3 mm), and 3.9 g (73%) of ethyl vinyl sulfone: b.p. 91.5-96° (4 mm); n_D^{20} 1.4670.

Oxidation with H_2O_2 in Presence of SeO_2. a) Ethyl vinyl sulfide (8.8 g, 0.1 mole) was added to a solution of 1.0 g of SeO_2 in 40 ml of t-butyl alcohol (b.p. 79-81° n_D^{20} 1.3856). Hydrogen peroxide (11.5 g, i.e., 0.22 mole, of 75% solution) was diluted with cooling with 10 ml of t-butyl alcohol and added dropwise with stirring at such a rate that the temperature of the reaction mixture did not exceed 60-65° (external cooling). The mixture was then heated further for four hours at 60-70°. To free it from SeO_2, the reaction mixture was passed twice though a column of basic ion-exchange resin (e.g. EDE-10 II) *; the resin was washed with ether. The

* It is somewhat less convenient to remove SeO_2 by passing the reaction mixture through a $CaCO_3$ column: for this purpose it is necessary first to distill off the alcohol and dilute the mixture with ether.

mixture was dried with sodium sulfate, and solvents were vacuum-distilled off. The only reaction product isolated was ethyl vinyl sulfone, which amounted to 8.5 g (71%); b.p. 87-88° (2 mm); n_D^{20} 1.4635 (residue in flask about 1 g). Table 6 shows the products of the oxidation of ethyl vinyl sulfide in t-butyl alcohol in presence of various amounts of SeO_2.

b) By the oxidation of 10.2 g (0.1 mole) of propyl vinyl sulfide with 11 ml of 75% H_2O_2 (0.22 mole of H_2O_2) in 40 ml of t-butyl alcohol in presence of 1.0 g of SeO_2 we obtained 8.8 g (66%) of propyl vinyl sulfone; b.p. 107-107.5° (5 mm); n_D^{20} 1.4643; d_4^{20} 1.1060. Found: C 44.50; 44.71; H 7.48; 7.64; S 23.58; 23.54%. $C_5H_{10}SO_2$. Calculated: C 44.77; H 7.52; S 23.80%.

c) Under the same conditions, by the oxidation of 11.6 g (0.1 mole) of butyl vinyl sulfide with 13.0 g of 64% H_2O_2 (0.27 mole) in 40 ml of t-butyl alcohol in presence of 1 g of SeO_2 we obtained 8 g (54%) of butyl vinyl sulfone, b.p. 116-117° and n_D^{20} 1.4620.

The authors thank P.P. Shorygin for advice in the spectrographic part of the work.

SUMMARY

1. The conditions were found for the selective oxidation of sulfur in vinyl sulfides with formation of sulfoxides and sulfones (50-70% yield).

2. The molecular refractions of vinyl sulfones and sulfoxides were determined; also, the character of the absorption in the ultraviolet and of the Raman spectra is discussed from the point of view of the electronic structures of the sulfoxide and sulfone groups.

3. The ultraviolet absorption spectra of vinyl sulfones were used as a criterion of purity.

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HYDROGENATION OF 2-ETHYLANTHRAQUINONE OVER RANEY NICKEL

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There is little information in the literature on the hydrogenation of anthraquinone and alkylanthraquinones over Raney nickel. In early work it was shown that anthraquinones are rapidly reduced to the corresponding 9, 10- anthradiols, and this is followed by slow hydrogenation of the side nuclei. Thus, in alkaline solution anthraquinone was hydrogenated to tetrahydro-9, 10-anthradiol [1]. For the cases of anthraquinone and the diacetyl derivative of 2-methyl-9, 10-anthradiol it was shown that reduction can go as far as octahydro-9, 10-anthradiol [2]. By long boiling of an alcoholic solution of the quinone with Raney nickel, anthraquinone and 2-methylanthraquinone were reduced to octahydroanthraquinones, and anthraquinone in an aqueous solution of caustic alkali was reduced to perhydro-9, 10-anthradiol [3].

There have recently appeared several patents on the hydrogenation of alkylanthraquinones to the hydroquinone or quinhydrone in connection with their application as hydrogen carriers in the industrially important process for the preparation of hydrogen peroxide [4-8]. In the present work we studied the hydrogenation of 2-ethylanthraquinone in presence of Raney nickel in dioxane, in a mixture of dioxane and 96% alcohol, and in N, N-dimethylformamide.

EXPERIMENTAL

Experimental Procedure and Conditions. 2-Ethylanthraquinone was hydrogenated with electrolytic hydrogen in a thermostated hydrogenation flask at 20° and atmospheric pressure with vigorous agitation (750 shakes per minute). The solvents used were dioxane, a 3: 5 mixture of dioxane and 96% alcohol, and N,N-dimethylformamide. Dioxane was first purified from peroxide by treatment with caustic alkali and distillation over sodium. For each experiment we took 2.37 g of 2-ethylanthraquinone in 40 ml of solvent (m.p. 107-108°). The literature [9] gives m.p. 108°. The Raney nickel was prepared by leaching a finely ground 1: 1 Ni–Al alloy with 20% aqueous sodium hydroxide at 50° and keeping the product for two hours at 105°. Apart from nickel, analysis of the catalyst showed the presence of 0.95% of Al, 0.8% of Fe, 0.8% of Cu, and traces of Sb, Pb, Sn, and Bi. The catalyst was weighed on a torsion balance under a layer of solvent [10, 11], transferred to a hydrogenation flask in a stream of hydrogen, washed with solvent while being shaken, and saturated with hydrogen. The portion of catalyst was used only once.

Effect of the Nature of the Solvent. Figures 1-3 show the kinetic curves for the hydrogenation of 2-ethylanthraquinone. The rate of absorption of hydrogen $\frac{\Delta v_0}{\Delta t}$ (ml/min) is plotted as ordinate and the volume of hydrogen consumed $\Sigma\frac{v_0}{2}$ is plotted as abscissa. Figures 1-3 indicate that the form of the kinetic curve varies in the three solvents and varies also with change in the amount of catalyst. In dioxane, at low amounts of catalyst the absorption of the first molecular proportion goes at a diminishing rate, but at high amounts the rate is constant. In a mixture of dioxane and alcohol and in N,N-dimethylformamide in presence of low amounts of

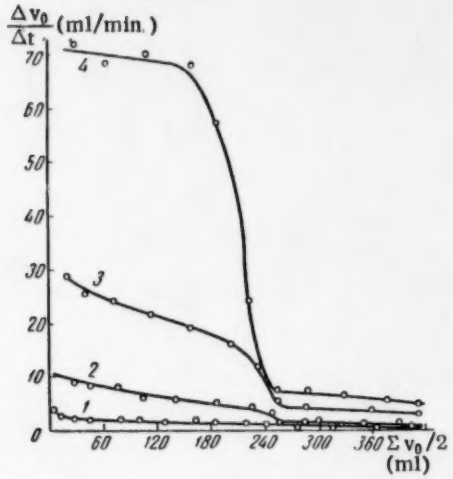

Fig. 1. Hydrogenation of 2-ethylanthraquinone in dioxane in presence of various amounts of catalyst: 1) 0.330 g; 2) 0.660g; 3) 1.3309; 4) 2.660.

catalyst hydrogenation proceeds in accordance with a zero-order equation, but in presence of high amounts the reaction accelerates appreciably toward the end of the absorption of the first molecular proportion of hydrogen.

The rate of addition of the first molecular proportion of hydrogen, which is at its least in the case of dioxane, rises sharply when the hydrogenation is carried out in a mixture of dioxane and alcohol. In N,N-dimethylformamide the reaction again proceeds at a higher rate. These differences in the rates of hydrogenation of 2-ethylanthraquinone are probably to be explained by the differences in the strength of the hydrogen-catalyst bond in different solvents and also by the magnitude of the dielectric constant of the medium, which is least for dioxane (dioxane 2.21, alcohol 24.3, N,N-dimethylformamide 36.7). It has been shown that the reduction of anthraquinone proceeds through an intermediate semiquinone form, whose stability increases with decrease in the dielectric constant of the medium [12].

The extent of the hydrogenation of 2-ethylanthraquinone also depends on the nature of the solvent. In N-N-dimethylformamide only one molecular proportion of hydrogen is absorbed, and the reaction then stops. It is clear that in this solvent 2-ethylanthraquinone is selectively hydrogenated to the hydroquinone. On the kinetic curves for the hydrogenation of the quinone in dioxane and in a mixture of dioxane and alcohol there is a sharp break corresponding to the moment at which one molecular proportion of hydrogen is absorbed. However, the reaction does not stop, and the hydrogenation of the side aromatic nuclei of 2-ethylanthraquinone proceeds at an appreciable rate. The hydrogenation of the quinone proceeds least selectively in dioxane.

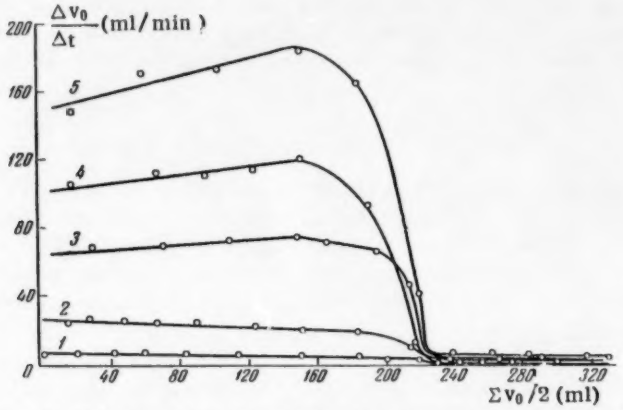

Fig. 2. Hydrogenation of 2-ethylanthraquinone in a mixture of alcohol and dioxane in presence of various amounts of catalyst: 1) 0.05 g; 2) 0.114 g; 3) 0.228 g; 4) 0.456 g; 5) 0.700 g.

The selective action of the catalyst in N,N-dimethylformamide is probably due to the selective absorption of the quinone at its quinone group. It is known, for example, that in presence of certain nitrogen-containing substances an acetylenic bond can be selectively hydrogenated to an ethylenic bond and a conjugated diolefin to a monoolefin over Raney nickel [13].

In the investigation of the hydrogenation of 2-ethylanthraquinone (0.73 g) in dioxane (20 ml) over Raney nickel (1 g) in presence of a small amount of pyridine (0.2 ml) we found that the reaction rate is greatly reduced

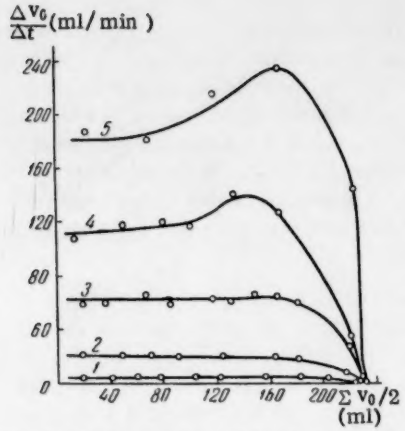

Fig. 3. Hydrogenation of 2-ethylanthraquinone in N,N-dimethylformamide in presence of various amounts of catalyst: 1) 0.050 g; 2) 0.155 g; 3) 0.302 g; 4) 0.604 g; 5) 1.220 g.

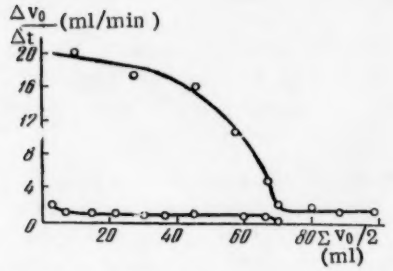

Fig. 4. Effect of pyridine on the hydrogenation of 2-ethylanthraquinone in dioxane: Upper curve: hydrogenation without pyridine. Lower curve: hydrogenation with 1% of pyridine.

and ceases after the absorption of one molecular proportion of hydrogen (Fig. 4). In contrast, in N,N-dimethylformamide hydrogenation proceeds not only selectively, but also very rapidly (much faster than in dioxane). The treatment of the catalyst with pyridine to prevent hydrogenation of the nucleus of 2-ethylanthraquinone was proposed also in one of the patents [8].

Effect of the Amount of the Catalyst. The table and Fig. 5 show the relation of the specific activity of the catalyst to its amount in the hydrogenation of 2-ethylanthraquinone to the hydroquinone. The specific activity was characterized by the initial rate of addition of hydrogen (ml/min) referred to 1 g of catalyst. Analogous results were obtained for rates at the moment of the absorption of one-half a molecular proportion of hydrogen. From Fig. 5 and the table it can be seen that with increase in the amount of catalyst its specific activity increases greatly in all three solvents. This is an interesting fact, for it is known that the rate of reaction proceeding in the kinetic region is usually directly proportional to the amount of catalyst, i.e., its specific activity remains constant. It is seen from Fig. 5 that the curve for the relation of the specific activity of the catalyst to its amount in the hydrogenation of the quinone in N,N-dimethylformamide or in a dioxane-alcohol mixture passes through a maximum at 0.2-0.3 g of catalyst. It is evident that for large amounts of catalyst the effect of diffusion on the rate of the process begins to have an effect. It was shown by special experiments that for amounts of catalyst corresponding to the rising branch of the curve the reaction rate did not depend on the degree of agitation when this was more than 300-400 shakes per minute. It was found that the maximum specific activity for small amounts of catalyst was observed only when the reaction was carried out in N,N-dimethylformamide or in alcohol-dioxane mixture in which the rate of hydrogenation was very high. In dioxane the rate of hydrogenation was considerably lower, and the maximum (not shown in Fig. 5) was attained only with ten times the amount of catalyst.

DISCUSSION OF EXPERIMENTAL RESULTS

The usual dependence of the specific activity of the catalyst on its amount in the reaction investigated may be explained by the

In dioxane			In alcohol-dioxane mixture			In N,N-dimethylformamide		
amount of catalyst (g)	rate of absorption of hydrogen	specific activity	amount of catalyst (g)	rate of absorption of hydrogen	specific activity	amount of catalyst (g)	rate of absorption of hydrogen	specific activity
0,330	2,5	8	0,056	7	125	0,050	5	100
0,660	10	15	0,114	24	210	0,155	21	137
1,330	27	20	0,228	68	298	0,302	63	207
2,660	70	31	0,456	105	230	0,604	114	188
			0,700	155	221	1,220	182	149

chemical nonuniformity of the hydrogen sorbed by the catalyst. 2-Ethylanthraquinone is very readily hydrogenated to the hydroquinone, so that with small amounts of catalyst not only the most active hydrogen is required, but also hydrogen that is more strongly bound to the catalyst. When the amount of catalyst relative to the amount of the quinone to be hydrogenated is increased, the most active and readily replaced hydrogen will, in

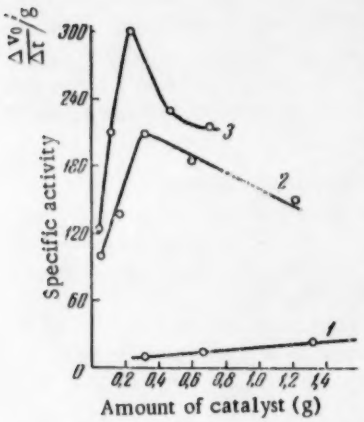

Fig. 5. Relation of the specific activity of the catalyst to its amount: 1) in dioxane; 2) in N, N-dimethylformamide; 3) in the alcohol-dioxane mixture.

the main, be consumed, which will lead to increase in the specific activity of the catalyst. Increase in the specific activity of the catalyst with increase in its amount was observed also in the hydrogenation of 1-hexyne [14]. Such a relation is evidently characteristic only for compounds that are readily hydrogenated and are able to extract considerable amounts of hydrogen from a catalyst of high activity. Hence, the hydrogenation of the nucleus of 2-ethylanthraquinone in dioxane, which occurs with considerably more difficulty, is accelerated to an extent that is proportional to the amount of catalyst (Fig. 1).

The ability of 2-ethylanthraquinone to react with a considerable part of the hydrogen sorbed in Raney nickel was confirmed by us experimentally. From 1 g of catalyst 2-ethylanthraquinone extracts 60-70 ml of hydrogen, after which with the aid of p-benzoquinone a further 50-60 ml of hydrogen can be extracted. This is also in accord with potentiometric measurements carried out by us by the method of Sokol'skii and Druz' [15] during the hydrogenation of 2-ethylanthraquinone in an alcohol-dioxane mixture. On addition of the quinone the potential of the catalyst relative to a saturated calomel electrode fell sharply and then rose rapidly and remained constant during further reaction until one molecular proportion of hydrogen had been absorbed. The fall in potential was 140-160 mv. At the moment corresponding to the absorption of the first molecular proportion of hydrogen the potential again rose suddenly, and the further slow hydrogenation of the side nuclei occurred at a potential close to the reversible value. The jump in potential at the moment at which the absorption of the first molecular proportion of hydrogen is complete is evidently due to the complete conversion of the quinone into the hydroquinone; it coincides with the break on the kinetic curves for the absorption of hydrogen. In N,N-dimethylformamide hydrogenation again proceeds at a constant potential, but the fall in the potential of the catalyst during the reaction is greater (180-210 mv).

It is interesting to compare the hydrogenation of 2-ethylanthraquinone with the reduction of p-benzoquinone over Raney nickel. It has been shown [16] that p-benzoquinone can extract almost the whole of the hydrogen from a nickel catalyst, which is thereby deactivated. Correspondingly, the fall in the potential of the catalyst in the hydrogenation of benzoquinone (600-700 mv) is considerably greater [17]. 2-Ethylanthraquinone is hydrogenated at a high rate even in presence of very small amounts of Raney nickel (0.05 g) containing less than 3% of the hydrogen theoretically required for the hydrogenation of 2.37 g of the quinone. Hence, reaction proceeds at the expense of hydrogen from the gas phase. The observed value of the fall in the potential of the catalyst in an alcohol-dioxane mixture is close to the normal oxidation-reduction potential [18] of anthraquinone and 2-methylanthraquinone (150-157 mv) in alcohol, which probably differs only a little from the potential for 2-ethylanthraquinone. An analogous coincidence of the normal oxidation-reduction potential and the fall in the potential of the catalyst during hydrogenation was observed also for p-benzoquinone [17].

SUMMARY

1. A study was made of the hydrogenation of 2-ethylanthraquinone at 20° in dioxane, an alcohol-dioxane mixture, and N,N-dimethylformamide in presence of Raney nickel.

2. In N,N-dimethylformamide addition of only one molecular proportion of hydrogen occurs. In dioxane and an alcohol-dioxane mixture the aromatic side nuclei of 2-ethylanthraquinone are also hydrogenated at an appreciable rate.

3. With increase in the amount of catalyst its specific activity in the hydrogenation reaction increases. This behavior is probably associated with the chemical nonuniformity of hydrogen in a highly active catalyst.

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ACTIVITY AND SELECTIVITY OF A ZINC CATALYST IN THE HYDROGENATION OF AN ACETYLENIC TO AN ETHYLENIC BOND

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The selective hydrogenation of a triple carbon-carbon bond to a double bond has been the subject of many investigations. The selectivity of the process depends on many factors: the natures of the catalyst and compound to be hydrogenated, the pressure, and the temperature have particularly great effects. In the present work we have studied for the first time the possibility of the selective hydrogenation of a triple bond in presence of a zinc catalyst for the cases of acetylene, diphenylacetylene, and 2-methyl-3-butyn-2-ol.

Over platinum, nickel, cobalt, copper, and their alloys, acetylene is hydrogenated nonselectively [1-5]. A palladium catalyst, particularly when the palladium is in a colloidal form, shows selectivity [6-7]. A good yield of ethylene is obtained over a palladium catalyst treated with lead acetate [8]. The selective hydrogenation of diphenylacetylene to stilbene was recently effected over Raney nickel poisoned with pyridine [9].

In presence of platinum and Raney nickel catalysts, dialkylethynylmethanols are hydrogenated nonselectively: after the absorption of one molecular proportion of hydrogen a mixture is obtained of the original, the ethylenic, and the saturated alcohols. Over palladium on calcium carbonate the process proceeds stagewise and, if the reaction is stopped after the absorption of one molecular proportion of hydrogen, the dialkylvinylmethanol is obtained in almost theoretical yield [10].

The results of the present work show that zinc has considerable activity in promoting the addition of hydrogen to an acetylenic bond. It is particularly interesting that over this catalyst at low temperature the acetylenic bond is selectivity hydrogenated to an ethylenic bond.

EXPERIMENTAL

Hydrogenation of Acetylene. A skeletal zinc catalyst was prepared by leaching a 1:1 (by weight) Zn–Al alloy with 3% aqueous sodium hydroxide [11]. The amount of catalyst was 125 ml and the height of the layer was 135 mm. The reaction was carried out under flow conditions. The gas used contained about 98% of acetylene and was first passed through 10% aqueous caustic alkali, chromic acid mixture, activated charcoal, and calcium chloride to free it from possible impurities, such as carbon dioxide, hydrogen cyanide, hydrogen sulfide, and moisture. A previous prepared and analyzed mixture of acetylene and hydrogen was fed to the catalyst through a flowmeter. Before the start of the experiment the system was purged with the gas mixture for 15 minutes. The gaseous products were collected in a Patrikeev automatic gas meter [12] and, like the original gas mixture, were analyzed chromatographically [13, 14]. Separation was effected at room temperature in silica gel and charcoal columns. Hydrocarbon gases separated in the first, and hydrogen was determined in the second. Fig. 1 gives the chromatograms (b) and (c) of the gaseous products formed in Experiments 3 and 4 (Table 1). For comparison we give the graduation curve (a) for an artifically prepared mixture of ethane, ethylene, acetylene, and hydrogen (19.8, 17.2, 21.5, and 39.0%, respectively) together with 2.3% of air.

TABLE 1

Expt.	Temp. (°C)	Rate of passage of gas mixture (ml/min.)	Acetylene content of mixture (% by vol.)	Content (%) in gaseous products of		Fraction (%) of acetylene consumed in side reactions	Yield of ethylene	
				acetylene	ethylene		(% on amt passed)	(% on amt. that reacted)
1	65	20	31,0	25,4	2,3	15	7	32
2	75	20	31,0	18,4	6,7	24	20	46
3	85	20	32,0	17,5	10,8	20	30	60
4	100	20	26,4	8,2	11,0	32	38	56
5	110	20	26,4	3,2	11,3	46	41	53
6	100	20	3,4	1,2	1,5	21	43	65
7	100	50	8,9	4,3	2,1	28	23	51
8	100	20	8,9	7,55	0,4	11	4	28
9	100	20	8,9	5,8	0	35	—	—
10	100	20	9,3	7,2	0,4	37	4	54

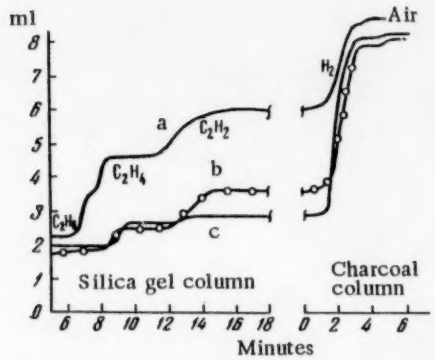

Fig. 1. Chromatograms: a) artificial mixture; b) gaseous reaction products of Expt. 3, Table 1; c) gaseous reaction products of Expt. 4, Table 1.

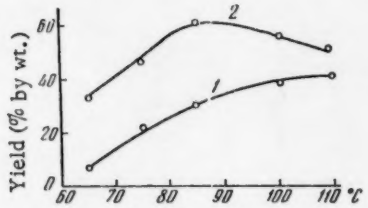

Fig. 2. Hydrogenation of acetylene at various temperatures: 1) yield of ethylene on amount passed; 2) yield on acetylene that reacted.

The results of experiments on the hydrogenation of acetylene over a zinc catalyst at various temperatures are given in Table 1. The most interesting result is that in all experiments the chromatograms showed the complete absence of ethane among the gaseous reaction products. It may be assumed that in the process investigated the consumption of hydrogen is associated mainly with the hydrogenation of acetylene and is approximately equal to the volume of ethylene formed. Taking account of this hydrogen, we calculated the amount of unchanged acetylene and also the extent to which acetylene was converted into ethylene. The fraction of the acetylene consumed in other reactions was calculated by difference. From the results it follows that much of the acetylene (about 50% of that which reacted) was consumed in reactions accompanying the hydrogenation. It will be seen from Experiments 1-5 that with rise in temperature the acetylene content of the mixture falls and the yield of ethylene correspondingly rises (Fig. 2) and at 100° attains 38% on the amount passed and 56% on the amount that reacts. However, already at 100° and 110° the yield of ethylene, calculated on the acetylene that reacts, diminishes, i.e., the reactions accompanying hydrogenation become still more marked.

It is known that the hydrogenation of acetylene is a strongly exothermic process. In this connection we carried out an experiment in which the acetylene content of the gas mixture was considerably less (3.4%). It will be seen that under conditions of high dilution the consumption of acetylene in the accompanying reactions fell greatly, but the yield of ethylene was only a little higher. In Expt. 7 the gas mixture was passed at a high space velocity: the yield on the amount passed was less, but the yield on the acetylene that reacted was unchanged, i.e., the extent to which side reactions occurred was not reduced. In Expt. 8 a sample of gas for analysis was taken after 3.5 hours from the start of the work of the catalyst. The yield of ethylene was found to be

TABLE 2

Expt.	Temp. (°C)	Consumption of hydrogen (ml) in the hydrogenation of 5 ml of catalyzate		Amt. found in catalyzate (%)	
		in absence of pyridine	in presence of pyridine	of diphenyl-acetylene	of stilbene
—	—	70,4*	35,6*	100	0
1	60	63,4	28,7	83,1	17,0
2	75	57,6	23,3	65,8	31,2
3	85	43,8	8,9	25,3	73,9
4	95	36,5	3,4	9,6	83,3
5	110	30,4	0	0	85,8
6	120	27,4	0	0	77,8

* Consumption of hydrogen in the hydrogenation of 5 ml of the original solution of diphenylacetylene in cumene.

TABLE 3

Expt.	Temp. (°C)	Consumption of hydrogen in the hydrogenation of 1.17 g of catalyzate (ml)	Consumption of 0.1 N NaOH (ml)*	Amount found (%) in catalyzate	
				2-Methyl-3--butyn-2-ol	2-Methyl-3-buten-2-ol
1	70	62,4	17,4	100	0
2	90	61,8	17,4	100	0
3	100	54,5	12,9	74,1	27,7
4	110	41,0	5,4	31,0	71,4
5	120	27,7	0,5	2,9	83,5
6	140	13,1	0	0	42,5
7	160	6,9	0	0	22,1

* The consumption of alkali in the neutralization of the nitric acid liberated by the action of aqueous silver nitrate on 1.46 g of the original alcohol or the catalyzate.

very low, probably because the catalyst was deactivated during the process. In Expt. 9, simultaneously with the gas mixture, water was passed over the catalyst at 1 ml/min. Under these conditions only the "side" reactions occurred: ethylene was not formed at all. Similar results were obtained on dilution with ethanol in Expt. 10. In the determination of the amount of unchanged acetylene in this experiment, a correction was made for the content of acetylene (8.4 ml) in 15 ml of alcohol used for washing the catalyst.

Hydrogenation of Diphenylacetylene. A solution of chemically pure diphenylacetylene (m.p. 64°) in cumene was used. The rate of feed was 0.7 ml of 5.6% by weight solution per minute. Each experiment lasted for about 30 minutes. The direction of the process was judged from the change in the unsaturation of the catalyzate. Its total unsaturation (content of ethylenic and acetylenic bonds) was determined from the volume of hydrogen consumed in the hydrogenation of an aliquot of the catalyzate in presence of Raney nickel. For the determination of the C ≡ C bond in the catalyzate we made use of the fact that in presence of pyridine over Raney nickel at 20° diphenylacetylene is selectively hydrogenated to stilbene [9]. It was shown by a special experiment that under these conditions stilbene is definitely not hydrogenated. Hence, the consumption of hydrogen in the hydrogenation of an aliquot of the catalyzate in absence of pyridine determines the total content of diphenylacetylene and stilbene, whereas, when pyridine is present, it determines diphenylacetylene only. The stilbene content of the catalyzate was calculated by difference. An example of the calculation for the results of Expt. 3 (Table 2): For the hydrogenation of 5 ml of solution containing 0.28 g of diphenylacetylene, 70.4 ml of hydrogen was required. For the hydrogenation of 5 ml of catalyzate, 43.8 ml of hydrogen was

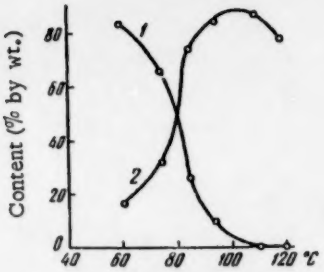

Fig. 3. Hydrogenation of diphenylacetylene at various temperatures: 1) diphenylacetylene content of the catalyzate; 2) stilbene content.

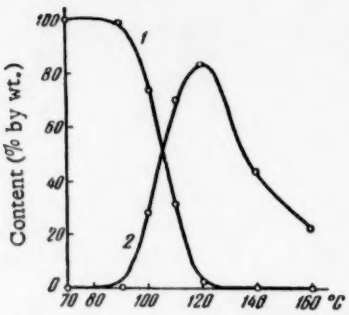

Fig. 4. Hydrogenation of 2-methyl-3-butyn-2-ol at various temperatures: 1) 2-methyl-3-butyn-2-ol content of the catalyzate; 2) 2-methyl-3-buten-2-ol content.

required, but the amount was reduced to 8.9 ml in presence of pyridine. Hence, $\frac{8.9 \cdot 2 \cdot 100}{70.4} = 25.8\%$ of the diphenylacetylene did not react. In the hydrogenation of the double bond 43.8−17.8 = 26 ml of hydrogen was consumed, which corresponds to 73.9%.

Table 2 shows that over a zinc catalyst diphenylacetylene is hydrogenated already at 60°. With rise in temperature the diphenylacetylene content of the catalyzate falls sharply and its stilbene content increases correspondingly. At 110° diphenylacetylene is absent from the catalyzate and the stilbene content also begins to fall. From the catalyzates of Experiments 4 and 5 stilbene was isolated after solvent was distilled off; after recrystallization it melted at 116°. For stilbene the literature [15] gives m.p. 120°. The low melting point of the product is probably to be explained by a little diphenylacetylene impurity.

Hydrogenation of 2-Methyl-3-butyn-2-ol. The reaction was carried out in absence of solvent. We used freshly distilled 2-methyl-3-butyn-2-ol (b.p. 102°; d_4^{20} 0.8617, n_D^{20} 1.4203); the rate of feed was 1.4 ml/min. Each experiment lasted about one hour. The total content of 2-methyl-3-butyn-2-ol and 2-methyl-3-buten-2-ol in the catalyzate was determined from the volume of hydrogen consumed in the hydrogenation of an aliquot (1.17 g) in presence of Raney nickel at 20°. The content of unchanged 2-methyl-3-butyn-2-ol in the catalyzate was determined by Kondrat'ev's method [16] from the amount of acid liberated in the reaction of an aliquot of the catalyzate with aqueous silver nitrate. The acid was titrated with 0.1 N NaOH in presence of Methyl Orange. As an example of the calculation we shall take Expt. 3 (Table 3). The amount of unchanged 2-methyl-3-butyn-2-ol found in the catalyzate was 74.1%, which corresponds to 45.9 ml of hydrogen. Hence, for the hydrogenation of the 2-methyl-3-buten-2-ol formed, 54.5−45.9 = 8.6 ml of hydrogen was consumed, which corresponds to $\frac{8.6 \cdot 100}{31.0} = 27.7\%$.

Table 3 shows that reaction did not go at 70-90°. With rise of temperature the content of 2-methyl-3-butyn-2-ol began to fall and a corresponding amount of 2-methyl-3-buten-2-ol was formed. At 120° only 2.9% of 2-methyl-3-butyn-2-ol remained in the catalyzate, and the content of 2-methyl-3-buten-2-ol attained 83.5%. In the temperature range 100-110° the total content of 2-methyl-3-butyn-2-ol and 2-methyl-3-buten-2-ol corresponded to 100% of the original alcohol, i.e., no other processes occurred. At higher temperature the content of ethylenic bonds in the catalyzate began to fall and the total unsaturation of the catalyzate fell sharply.

Hence, at temperatures below 100° a zinc catalyst has considerable activity and specificity in the hydrogenation of diphenylacetylene and 2-methyl-3-butyn-2-ol.

For the determination and interpretation of the chromatograms we express our thanks to T.K. Lavrovskaya.

SUMMARY

1. A study was made of the activity and selectivity of a zinc catalyst in the hydrogenation of the triple carbon-carbon bonds of acetylene, diphenylacetylene, and 2-methyl-3-butyn-2-ol.

2. Acetylene is hydrogenated only as far as ethylene. About one half-of the acetylene that reacts is consumed in side reactions.

3. Below 100° diphenylacetylene and 2-methyl-3-butyn-2-ol are hydrogenated selectively to stilbene and 2-methyl-3-buten-2-ol, respectively.

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EFFECT OF THE SEQUENCE OF THE INTRODUCTION OF FOREIGN SUBSTANCES ON THE ACTION OF PAPAIN

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The properties of enxymes vary greatly with the nature of their substrate. Change of substrate results in the appearance of various complexes of the substrate with other substances, through this does not deprive the substrate of all its properties as a substrate of this enzyme. An example of such change in enzymic properties is provided by the proteolytic enzymes, in which proteins play the part of substrate.

Because of the high reactivity of the protein molecule, it is able to undergo various changes, in particular reaction with such compounds as lipides [1], polysaccharides [2], ionic substances [3], detergents [4], nucleic acids [5], and other proteins [6]; proteolytic enzymes are rarely found in the free state in biological systems. This leads to the formation of complex protein molecules in which the functions of the protein and nonprotein parts of these complexes depend on the associated chemical groups and their effects on the macrostructure of the protein and on the chemical bonds taking part in the formation of these complexes. These bonds may be covalences, or they may be formed by electrostatic or van der Waals interaction. Such protein complexes stimulate enzymic processes; their investigation can throw much light on the way in which the primary proteins may have evolved.

In the investigation of inhibitors for trypsin, Viswanatha and Irvin found that a considerable change was produced in the enzymic properties of trypsin by the addition of an inhibitor to the enzyme on its substrate [7]. It is generally known that in organisms the interaction of pharmacological agents with proteins reduces the physiological activity of various drugs. For example, blood plasma lowers the activity of penicillin [8], and the antibacterial activity of oleic acid toward tuberculosis bacilli is lowered considerably by the introduction of serum albumin [9].

Deborin showed [10] that ergosterol reacts with trypsin and also with serum albumin. However, the trypsin-ergosterol complex reacts with serum albumin in a way which differs from that in which the serum albumin - ergosterol complex reacts with trypsin, i.e., the order of the addition of ergosterol to the reaction mixture of enzyme-substrate is an important factor.

Also, we have observed that certain amines have a great effect on the reaction of papain with a substrate consisting of a suspension of flour from the grains of Cicer arietinum in water or of a solution of casein, but the effect varies in character according to the procedure adopted: admixture of the enzyme followed by reaction with casein (or a suspension of flour from the grains of Cicer arietinum) as compared with the preparation of the same mixture in which casein (or Cicer arietinum flour suspension) reacts with the amine and reaction is then carried out with papain.

TABLE 1

Difference in the Proteolytic Properties of Papain Observed When the Order of Introduction of the Amine is Changed (Mixture at pH 7.09) (Buffer: boric acid - borax; substrate: suspension of flour from grain of Cicer arietinum in water)

No.	Amine added	Amt. (ml) of 0.05 N NaOH required to neutralize 5 ml of mixture before addition of formaldehyde					
		0 hrs.	24 hrs.	48 hrs.	72 hrs.	96 hrs.	120 hrs.
1	Control expt.	0,65	0,95	0,95	0,60	0,75	0,45
2	Aniline	1,05	0,55	0,50	0,30	0,50	0,50
3	Aniline hydrochloride	1,0	0,60	0,45	0,40	0,45	0,55
4	Aniline sulfate	1,0	0,80	0,45	0,45	0,55	0,60
5	Triethylamine	0,80	0,40	0,25	0,10	0,35	0,15
6	Aniline	0,85	0,50	0,45	0,40	0,55	0,45
7	Aniline hydrochloride	0,90	0,65	0,45	0,45	0,40	0,60
8	Aniline sulfate	1,0	0,80	0,70	0,45	0,60	0,60
9	Triethylamine	0,45	0,30	0,15	0,15	0,20	0,20
		After addition of formaldehyde					
1	Control expt.	0,40	0,60	0,30	0,90	0,75	0,70
2	Aniline	0,20	0,55	0,40	0,70	0,90	0,70
3	Aniline hydrochloride	0,15	0,70	0,25	0,75	0,55	0,50
4	Aniline sulfate	0,15	0,45	0,50	0,75	0,50	0,35
5	Triethylamine	0,10	0,70	0,70	0,70	0,50	0,35
6	Aniline	0,30	0,55	0,60	0,85	0,55	0,60
7	Aniline hydrochloride	0,35	0,65	0,80	0,85	0,70	0,75
8	Aniline sulfate	0,25	0,50	0,60	0,95	0,50	0,80
9	Triethylamine	0,30	0,55	0,60	0,85	0,40	0,40

Note: The temperature during the titration varied in the range 25-27°.

EXPERIMENTAL

The following solutions were prepared:

Substrate. Suspension of flour from the grain of Cicer arietinum in water (Tables 1 and 2): The flour (25 g) was shaken with 500 ml of distilled water, and the mixture was covered with a layer of toluene. The solution was kept for 30 minutes. The upper part of clear liquid was decanted through filter paper.

Casein solution (Tables 3, 4, and 5): Casein (25 g) was boiled in CO_2-free water in a beaker and two drops of phenolphthalein were added. The mixture was titrated with sodium hydroxide solution (about 0.1 N) until a pale-pink color appeared. The solution was cooled and transferred to a 500-ml measuring flask. It was made up to volume with distilled water.

Enzyme. Papain (0.5 g) was introduced into a 500-ml measuring flask; the flask was filled to the mark with hydrogen sulfide solution. The contents were carefully shaken and kept for ten minutes. For use, the upper layer of clear liquid was taken.

Hydrogen Sulfide Solution. A fresh solution was prepared as required by passing hydrogen sulfide through distilled water for one hour.

Buffer Solutions. Boric acid - borax (see Tables 1 and 2):

	pH 7.09	pH 8.08
Boric acid (0.2 M)	18.8 ml	14.0 ml
Borax (0.05M)	1.2 ml	6.0 ml

Potassium dihydrogen phosphate - borax (Tables 3, 4, and 5):

TABLE 2

Difference in the Proteolytic Properties of Papain Observed When the Order of Introduction of the Amine is Changed (Mixture at pH 8.08) (Buffer: boric acid - borax; substrate: suspension of flour from grain of Cicer arietinum in water)

No.	Amine added	Amt. (ml) of 0.05 N NaOH required to neutralize 5 ml of mixture before addition of formaldehyde					
		0 hrs.	24hrs.	48 hrs.	72 hrs.	96hrs.	120 hrs.
1	Control expt.	0,1	0,3	—	—	0,15	—
2	Aniline	0,3	0,25	0,2	0,5	0,10	—
3	Aniline hydrochloride	0,40	0,25	0,10	—	—	0,10
4	Aniline sulfate	0,30	0,35	0,10	—	0,10	—
5	Triethylamine	—	—				
6	Aniline	0,30	0,10				
7	Aniline hydrochloride	0,25	0,15	0,05			
8	Aniline sulfate	0,45					
9	Triethylamine						
		After addition of formaldehyde					
1	Control expt.	—	0,25	0,20	0,80	0,50	0,30
2	Aniline	0,05	0,20	0,30	0,50	0,40	0,25
3	Aniline hydrochloride	0,10	0,35	0,20	0,55	0,40	0,35
4	Aniline sulfate	0,05	0,25	0,35	0,65	0,50	0,30
5	Triethylamine	—	0,10	0,10	0,60	0,50	0,25
6	Aniline	0,05	0,40	0,60	0,60	0,30	0,25
7	Aniline hydrochloride	0,15	0,30	0,45	0,70	0,40	0,35
8	Aniline sulfate	0,15	0,30	0,50	0,75	0,50	0,45
9	Triethylamine	—	0,20	0,25	0,75	0,25	0,25

Note: The temperature during the titration varied in the range 25-27°.

	pH 6.0	7.0	8.0
KH_2PO_4 (0.1 M)	17.54 ml	12.46 ml	9.30 ml
Borax (0.05 M)	2.46 ml	7.54 ml	10.70 ml

Inhibitors. The following amines were used: aniline (in Flasks 2 and 6), aniline hydrochloride (in Flasks 3 and 7), aniline sulfate (in Flasks 4 and 8), and triethylamine (in Flasks 5 and 9).

In each case we used a 0.2% solution of the above-mentioned substance in 90% doubly distilled ethanol.

Preparation of Reaction Mixtures. We used the same method for all the experiments cited in the tables. Numbered conical flasks were taken, and into each of these the following solutions were introduced: 1) 20 ml of buffer solution (in accordance with the pH indicated in the tables); 2) 2 ml of alcoholic solution of inhibitor (in the control experiment 2 ml of alcohol was added); 3) and 4) in each of Flasks 1 to 5 we added 10 ml of substrate solution, and in the remainder (Flasks 6 to 9) we added 10 ml of enzyme solution. After 5 minutes, to each of the first group of flasks, which contained substrate solution, we added 10 ml of papain solution. To each of the second group (Flasks 6 to 9) we added 10 ml of substrate solution; 5) finally, to each flask, we added 10 ml of hydrogen sulfide solution. In all cases the reaction mixture was covered with a layer of toluene and the flask was corked.

Method of Titration. A 5-ml sample of the mixture was taken by pipet and titrated with 0.05 N (Tables 1 and 2) or 0.02 N (Tables 3, 4, and 5) NaOH to a pale-pink color with phenolphthalein. After the titration 5 ml of formaldehyde solution neutralized with dilute sodium hydroxide was added. If the color disappeared, it was restored by addition of 0.05 N (Tables 1 and 2) or 0.02 N (Tables 3, 4, and 5) NaOH, the volume taken being measured. Such titrations were carried out at definite intervals of time.

In Flasks 1 to 5 the order of addition was: 1) buffer solution; 2) inhibitor (or alcohol in the control experiment); 3) substrate; 4) enzyme; 5) hydrogen sulfide solution. In Flasks 6 to 9 the order was: 1) buffer solution; 2) inhibitor; 3) enzyme; 4) substrate; 5) hydrogen sulfide solution.

TABLE 3

Difference in the Proteolytic Properties of Papain Observed When the Order of Introduction of the Amine is Changed (Mixture at pH 6.0) (Buffer: potassium dihydrogen phosphate - borax; substrate: casein)

No.	Amine added	Amt. (ml) of 0.05 N NaOH required to neutralize 5 ml of mixture before addition of formaldehyde					
		0 hrs.	24 hrs.	48 hrs.	72 hrs.	96 hrs.	120 hrs.
1	Control expt.	10,65	10,60	11,20	10,45	9,10	7,05
2	Aniline	11,80	11,20	9,70	8,40	7,80	6,75
3	Aniline hydrochloride	10,60	8,50	8,70	7,20	5,70	5,50
4	Aniline sulfate	12,15	10,30	9,20	9,10	4,10	1,90
5	Triethylamine	11,85	8,90	8,65	8,90	6,60	1,70
6	Aniline	12,10	11,40	10,10	10,05	9,30	9,70
7	Aniline hydrochloride	11,15	10,50	9,90	5,30	3,20	6,20
8	Aniline sulfate	12,40	10,35	9,75	8,40	1,55	1,45
9	Triethylamine	10,80	10,30	9,45	9,80	3,00	1,90
		After addition of formaldehyde					
1	Control expt.	0,90	1,30	1,60	0,95	3,40	1,80
2	Aniline	—	1,30	2,60	3,00	1,40	2,95
3	Aniline hydrochloride	0,50	2,20	2,00	0,90	1,45	1,15
4	Aniline sulfate	—	0,65	1,55	1,30	1,25	0,45
5	Triethylamine	—	2,80	1,55	1,40	1,80	0,50
6	Aniline	—	0,50	2,40	2,75	0,90	1,55
7	Aniline hydrochloride	—	2,20	1,20	1,25	2,00	1,90
8	Aniline sulfate	—	1,30	1,40	3,05	2,20	1,65
9	Triethylamine	0,50	1,00	1,75	2,25	1,00	1,35

Note: The temperature during the titration varied in the range 29-32°.

TABLE 4

Difference in the Proteolytic Properties of Papain Observed When the Order of Introduction of the Amine is Changed (Mixture at pH 7.0) (Buffer: potassium dihydrogen phosphate - borax; substrate: casein)

No.	Amine added	Amt. (ml) of 0.05 N NaOH required to neutralize 5 ml of mixture before addition of formaldehyde					
		0 hrs.	24 hrs.	48 hrs.	72 hrs.	96 hrs.	120 hrs.
1	Control expt.	5,10	4,90	5,20	4,65	3,55	4,00
2	Aniline	3,50	3,70	4,85	4,60	2,20	3,80
3	Aniline hydrochloride	3,50	3,00	2,90	2,45	1,30	1,40
4	Aniline sulfate	3,10	4,65	4,50	3,50	2,85	1,00
5	Triethylamine	3,80	3,25	4,55	3,50	3,90	0,70
6	Aniline	4,30	1,60	3,70	1,70	0,70	0,75
7	Aniline hydrochloride	3,00	2,00	2,60	3,55	2,10	1,40
8	Aniline sulfate	3,30	0,65	1,30	1,70	1,70	0,90
9	Triethylamine	2,95	2,55	3,40	3,00	1,60	0,90
		After addition of formaldehyde					
1	Control expt.	—	1,60	2,10	1,45	2,15	1,30
2	Aniline	—	0,80	1,35	1,00	1,00	1,30
3	Aniline hydrochloride	0,65	1,75	1,05	1,15	2,40	0,90
4	Aniline sulfate	0,65	1,60	1,90	0,85	1,95	1,30
5	Triethylamine	0,50	1,35	1,35	1,75	2,00	1,30
6	Aniline	0,60	1,55	2,50	3,30	0,80	2,20
7	Aniline hydrochloride	0,40	1,55	2,70	0,80	1,40	0,90
8	Aniline sulfate	0,40	5,40	1,60	1,50	1,00	1,50
9	Triethylamine	0,60	2,95	1,70	1,70	1,70	2,20

Note: The temperature during the titration varied in the range 29-32°.

TABLE 5

Difference in the Proteolytic Properties of Papain Observed When the Order of Introduction of the Amine is Changed (Mixture at pH 8.0)(Buffer: potassium dihydrogen phosphate - borax; substrate: casein)

No.	Amine added	Amt. (ml) of 0.05 N NaOH required to neutralize 5 ml of mixture before addition of formaldehyde					
		0 hrs.	24 hrs.	48 hrs.	72 hrs.	96 hrs.	120 hrs.
1	Control expt.	2,35	2,50	2,40	1,50	0,75	0,85
2	Aniline	2,10	1,60	1,40	0,70	0,50	0,25
3	Aniline hydrochloride	2,70	1,15	1,00	0,70	0,50	0,35
4	Aniline sulfate	2,20	0,80	0,70	0,75	0,45	0,10
5	Triethylamine	1,70	1,50	1,50	1,40	1,10	1,00
6	Aniline	2,30	1,30	1,50	0,85	0,60	0,30
7	Aniline hydrochloride	1,60	1,20	2,00	0,40	1,45	0,50
8	Aniline sulfate	1,75	0,85	0,90	0,30	0,20	0,05
9	Triethylamine	1,50	1,30	0,80	0,40	0,60	0,35
		After addition of formaldehyde					
1	Control expt.	—	0,30	1,45	1,10	2,45	3,10
2	Aniline	—	0,90	2,20	1,85	1,60	2,20
3	Aniline hydrochloride	—	0,85	1,70	0,65	0,90	0,65
4	Aniline sulfate	—	1,50	0,85	1,25	1,10	1,15
5	Triethylamine	—	0,20	0,85	1,10	1,10	0,55
6	Aniline	—	0,70	2,50	1,35	0,90	1,55
7	Aniline hydrochloride	0,20	1,20	1,10	1,05	0,50	1,00
8	Aniline sulfate	—	0,90	1,80	1,05	0,90	2,30
9	Triethylamine	—	1,40	1,25	1,15	0,90	0,50

Note: The temperature during the titration varied in the range 29-32°.

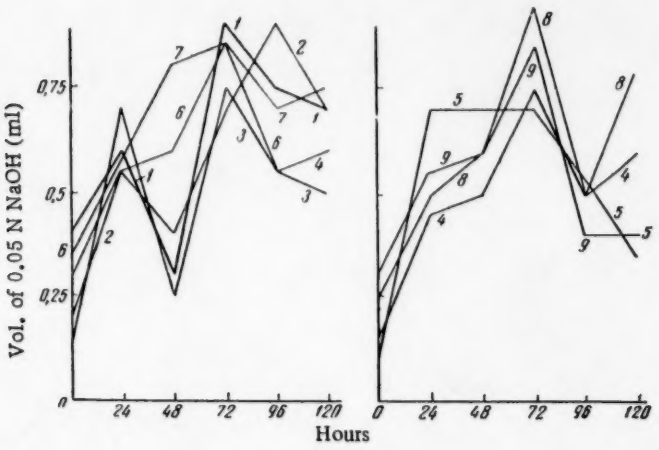

Fig. 1

DISCUSSION OF EXPERIMENTAL RESULTS

In the present work we studied the effects of aniline, aniline hydrochloride, aniline sulfate, and triethylamine on the hydrolysis of a suspension of the flour from the grain of Cicer arietinum in water (Tables 1 and 2) and of a casein solution (Tables 3, 4, and 5). Two sequences were used in the addition of the components of the reaction mixtures: 1) inhibitor, substrate, and then enzyme (for brevity this order will hereafter be denoted by IS), and 2) inhibitor, enzyme, and then substrate (this order will be denoted by IE).

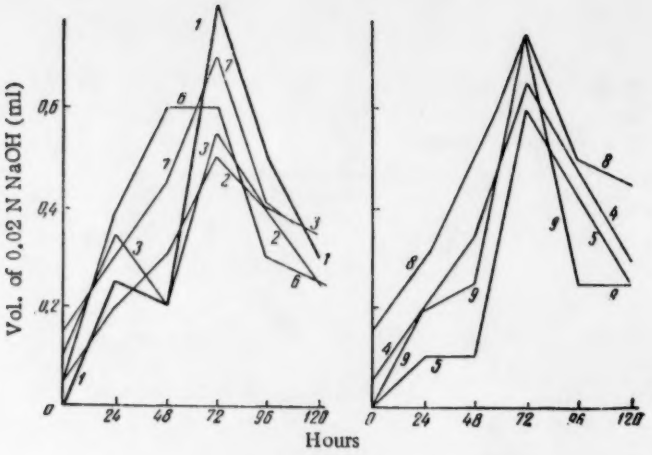

Fig. 2

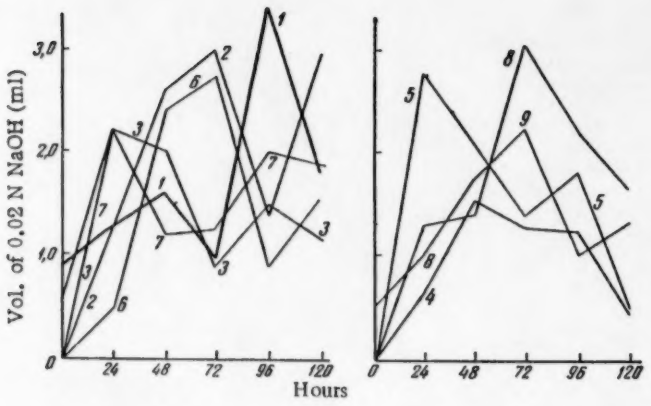

Fig. 3

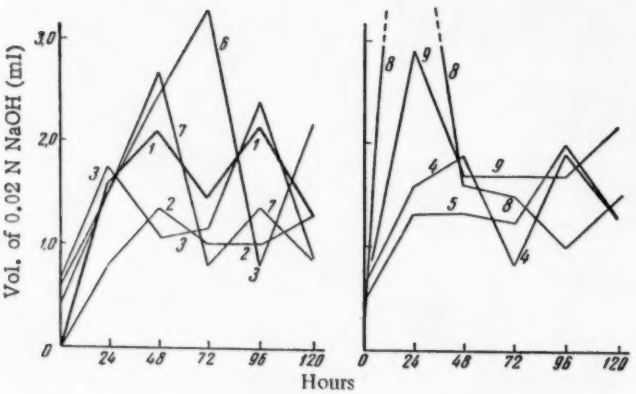

Fig. 4

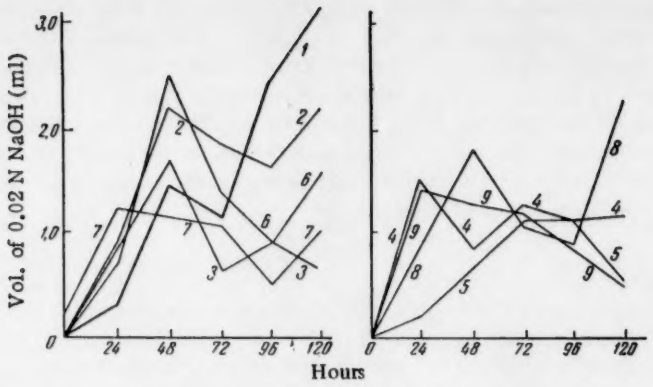

Fig. 5

When a boric acid - borax buffer of pH 7.09 was used (Fig. 1), it was found that aniline used in the sequence IS was more active as an inhibitor of the hydrolysis of a suspension of Cicer arietinum flour by papain than aniline used in the sequence IE. However, in the course of about 24 hours, the effect was reversed. This difference in the effect of change of order of addition attained its maximum after 24-72 hours. The activity of aniline hydrochloride used in the sequence IS compared well with the results of the control experiment, except in the case of the 48-hour result.

On the other hand, with the sequence IE aniline hydrochloride retarded the reaction. In the mixture containing aniline sulfate (sequence IE) the acidity was higher than in the mixture in which aniline sulfate and the substrate were the first components to be mixed. When triethylamine was used (sequence IS) in the period from 24 to 72 hours all proteolytic activity was at a standstill: it was found that after 72 hours the acidity, as measured after the addition of formaldehyde, fell gradually.

After the hydrolysis of the suspension of Cicer arietinum flour at pH 8.08 (boric acid - borax buffer) (Fig. 2), it was shown that the formation of amino acids in the control experiment was considerable (maximum at 72 hours) and that all the amines acted as inhibitors with respect to the activity shown in the control experiment.

In the case of aniline and its hydrochloride the retardation was greater with the sequence IS, except during the last 24 hours. This difference in activity for the two sequences attained its maximum at 48 hours both for aniline and for its hydrochloride. It was found also that aniline sulfate and triethylamine behave similarly, i.e., the sequence IS is the most favorable for the action of the inhibitor. An exception to this general rule was formed by the behavior of triethylamine during the last 48 hours.

When a potassium dihydrogen phosphate-borax buffer of pH 6.0 was used in the hydrolysis of casein with papain (Fig. 3), it was found that the proteolytic activity in the control experiment (after 96 hours) was greater than in the other experiments. For aniline the proteolytic activity with the sequence IS was always uniformly greater than when aniline was first mixed with the enzyme. When aniline hydrochloride was used with the sequence IS the extent of proteolysis was greater during the first 60 hours than when the sequence of addition was IE. However, during the last 60 hours the acidity of the reaction mixture diminished. A similar effect of difference in sequence on activity is shown particularly well in the case of aniline sulfate; here the maximum difference in activity resulting from difference in order of addition (IS or IE) is attained after 72 hours.

In the hydrolysis of casein in a potassium dihydrogen phosphate - borax buffer of pH 7.0 the proteolytic activity in the control experiment was not the greatest (Fig. 4). It was shown that all four compounds introduced in the order IE each had the effect that the proteolytic activity measured by the formaldehyde titration was greater than in the control experiment or in the corresponding mixture for which the order of addition was IS.

It is interesting to note that the four highest maxima belong to the group having the sequence IE: for aniline it occurs after 72 hours, for aniline hydrochloride after 48 hours, for aniline sulfate after 24 hours, and for triethylamine after 24 hours. The curves belonging to the group having the sequence IS occupy a lower place than those of the control experiments and of the corresponding mixtures with the sequence IE. When a

potassium dihydrogen phosphate - borax buffer of pH 8.0 was used (Fig. 5), proteolytic activity was at a maximum in the control experiment. However, it is rather strange that this should occur after 120 hours. In the case of aniline, change of order of addition had only a very slight effect on the amino acid content during the first 48 hours. After this the acidity fell more rapidly for the sequence IE than for the sequence IS. For aniline hydrochloride the higher activity was found for the sequence IS during the first 24 hours; after this, however, the difference became small. An exception was found in the 48-hour experiment, in which there was a higher acidity for the sequence IS than for the sequence IE. The behavior of aniline sulfate was in accord with the general rule, i.e., it acted as an inhibitor, and it was more effective when the enzyme was added to a mixture of substrate and inhibitor. The same applies to triethylamine.

SUMMARY

In general, aniline, aniline hydrochloride, aniline sulfate, and triethylamine act as inhibitors in the hydrolysis of casein or of a suspension of flour from grain of Cicer arietinum by means of papain. The order in which the enzyme and the substrate is added to the inhibitor often has a significant effect. As a rule, there is a greater retardation when the enzyme is added last to a complex of the substrate and the inhibitor.

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BRIEF COMMUNICATIONS

TEMPERATURE OF INITIAL HOT SPOTS DURING IMPACT INDUCTION OF AN EXPLOSION

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A hypothesis was put forward in [1] that the maximum temperature of hot spots during the detonation of an explosive by impact is limited by the melting point of the substance which depends on the pressure applied according to the approximate rule $T'_{melt} = T_{melt} + ap$, where T_{melt} is the melting point of the explosive at atmospheric pressure, T'_{melt} is the melting point at a pressure p, and a is a value which is approximately 0.02°/atm for all explosives. The formation of a hot spot is determined by two factors, namely, by pressure, which sets the maximum possible temperature, and by heat emission due to the action of external forces, which determines the actual temperature attained.

As a result of investigations [2-6], it seems to us that the following picture is the most probable one for the behavior of a sample of explosive under impact in an apparatus with free flow of material. At the beginning of the impact the separate crystals of the explosive are deformed plastically and fuse. The appearance of small amounts of the liquid phase results in the flow of the whole sample as a very viscous liquid. At this stage the distribution of pressures and rates appears as follows [7].

$$p = \frac{3u\eta}{h^3}(R^2 - r^2), \tag{1}$$

$$v_r = -\frac{3ur}{h^3}(z - h)z, \tag{2}$$

where u is the velocity of the falling weight, η is the viscosity coefficient of the mixture, R is the roller radius, h is the thickness of the explosive layer v_r is the radial flow velocity of the substance, and r and z are the axes of the cylindrical system of coordinates whose origin is at the center of the lower roller so that axis z coincides with the axis of the rollers.

At a sufficiently great initial energy of the weight, the change in its energy from the beginning of the impact to the explosion may be neglected. Let us assume that an explosion occurs when the thickness of the explosive layer differs little from the thickness of the explosive layer remaining on the rollers in the case of failure. In this case we may consider h constant if the initial thickness of the sample is close to that of the residual layer of explosive. The heating of a volume l^3 of explosive will be determined by the simple equation:

$$l^3 c\rho \frac{dT}{dt} = Kl^2(T - T_0) + q, \tag{3}$$

where K is the heat transfer coefficient, c is the heat capacity, ρ is the density of the explosive, and q is heat emission due to viscous forces. It is apparent that when $t = 0, T = T_0$. In calculating q is sufficient to consider only the component $\partial v_r/\partial z$, then

$$\dot{q} = \frac{l'\eta}{2}\left(\frac{3ur}{h^3}\right)(h-2z)^2$$

and equation (3) gives

$$T = T_0 + \frac{9\eta l u^2}{2Kh^4} r^2 \left(1-2\frac{z}{h}\right)^2 \left[1-\exp\left(\frac{Kt}{c\rho l}\right)\right].$$

An explosion occurs when a temperature T_*, equals to the critical one for dimension h, is reached. This temperature is reached at a weight velocity of u_* and pressure p_* which corresponds to a rise in the melting point of the explosive to T_* during the time τ_*. Considering that $z/h \cong 0$, and expanding the exponent into a series and taking the first term, from the preceding expression we obtain:

$$T_* - T_0 = \frac{9\eta R^2 \tau_* u_*^2}{2c\rho h^4}\xi_*^2. \qquad (4)$$

where the expression $\xi_* = r_*/R$, is introduced and with r_* equal to the distance from the center of the rollers to the spot where the explosion originates. According to (1), from the condition $T_* - T_{melt} = ap_*$ we have:

$$T_* - T_{melt} = \frac{3\eta a R^2}{h^3} u_* \left(1-\xi_*^2\right). \qquad (5)$$

As the viscosity coefficient is unknown, we must exclude it from (4) and (5). As a result we have:

$$\frac{1-\xi_*^2}{\xi_*^2} = \frac{3\tau_* u_* (T_* - T_{melt})}{2c\rho a h (T_* - T_0)} \qquad (6)$$

This expression includes only those values which may be measured experimentally and T_*.

We carried out experiments with tén,* hexogen, and octogen. The time from the beginning of the impact to the explosion was measured with a simple electrical circuit and an OK-17 M oscillograph. The value of ξ_* was measured from traces of burning remaining after the explosion on the surface faces of the rollers. Before an experiment the samples were compressed slightly to a thickness of approximately 0.2 mm. The experimental results are given in the table.

TABLE 1

Initial Temperatures of Hot Spots During Impact

Material	u_* in $\frac{cm}{sec}$	τ_* in μ'sec	ξ_*	T_* in °C
Ten	240	300	0,15	320
Hexogen	310	210	0,22	470
Octogen	310	150	0,26	500

The values of τ_* and ξ_* are the average of 4 to 5 experiments, and the scattering of the values was not greater than 20%. The initial velocity selected was such that the traces of burning would be most clearly seen. A 10 kg weight was used in the experiments.

The agreement of the values for T_* we calculated with the experimental and theoretical estimates of other authors [5, 6], shows that the scheme we adopted for the induction of an explosion under the given test conditions accurately reflects the most essential characteristics of the phenomenon and may be used for further study of this problem. On the other hand, this confirms the hypothesis on the role of pressure in the process of impact initiation put forward in [1].

SUMMARY

1. A method is proposed for calculating the initial temperature of hot spots during impact initiation of an explosion.

*This is a transliteration of Russian.

2. The initial temperatures of hot spots in the initiation of explosions in ten, hexogen, and octogen were calculated from experimental data.

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*Original Russian pagination. See C.B. translation.

ULTRAVIOLET AND VISIBLE ABSORPTION SPECTRA OF PYRIDINIUM CYCLOPENTADIENYLIDES

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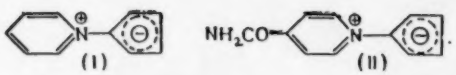
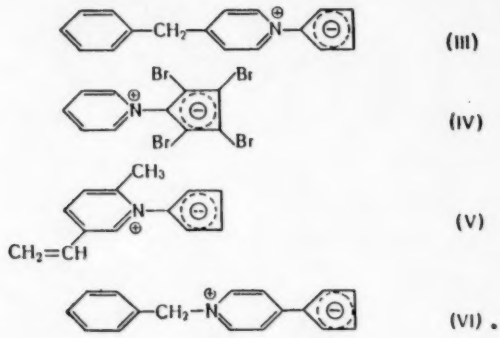
Cyclopentadienylides are a class of bipolar compounds which were discovered recently. A typical representative is pyridinium cyclopentadienylide (I), which was prepared by Lloyd and Sneezum [1] in 1955.



(I) (II)

The authors found that, depending on the solvent, this compound changes color from yellow to violet. Kosower and Ramsey [2] studied the ultraviolet and visible absorption spectra of pyridinium cyclopentadienylide (I) and 4-carbamidopyridinium cyclopentadienylide (II) and showed that they are characterized by a main absorption band and that the relation between the transition energy E_T (corresponding to the maximum absorption) and an empirical value z, connected with the polarity of the solvent, is linear.

We studied the absorption spectra* of γ-benzylpyridinium N-cyclopentadienylide (III) [3], 1-pyridinium 2,3,4,5-tetrabromocyclopentadienylide (IV) [4], 2-methyl-5-vinylpyridinium cyclopentadienylide (V)**, and N-benzylpyridinium γ-cyclopentadienylide (VI) [5] (Fig. 1).



(III)

(IV)

(V)

(VI).

*The absorption spectra were plotted on a fast-acting recording spectrovisor of V.I. Dianova-Klokov's design and on an SFD-1.

**The substance was not isolated in a pure state.

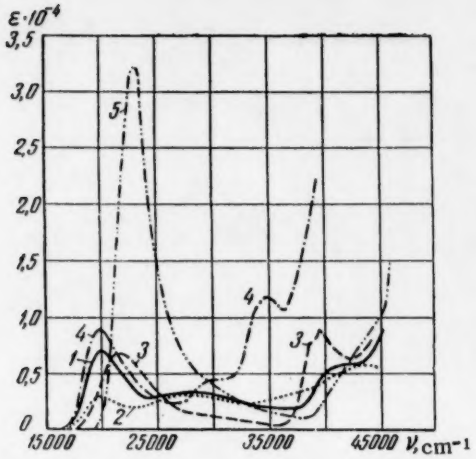


Fig. 1. Absorption spectra of cyclopentadienylides in ethanol: 1) pyridinium cyclopentadienylide; II) γ-benzylpyridinium N-cyclopentadienylide; III) pyridinium 2,3,4,5-tetrabromocyclopentadienylide; IV) 2-methyl-5-vinylpyridinium cyclopentadienylide; V) N-benzylpyridinium γ-cyclopentadienylide.

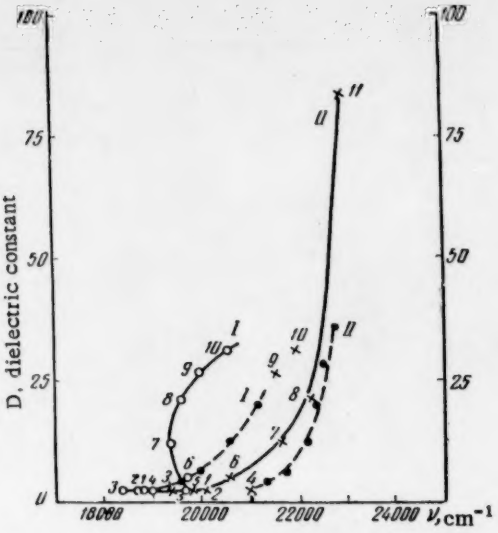


Fig. 2. Relation of position of absorption band maximum to dielectric constant: I) pyridinium cyclopentadienylide; II) pyridinium 2,3,4,5-tetrabromocyclopentadienylide. The figures denote the solvents given in the table (solid lines). The points without figures were obtained in aqueous dioxane solutions (broken lines).

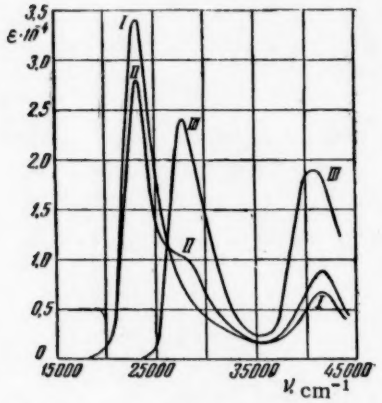
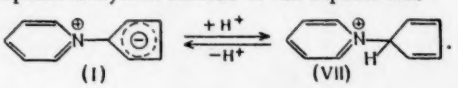


Fig. 3. Absorption spectra of N-benzylpyridinium γ-cyclopentadienylide: I) in alkaline methanol (0.5 N NaOH); II) in methanol; III) in acid methanol (1 : 9).

As with (I), substances, (III), (IV), and (V) were characterized by a main absorption band in the region of 18,000-21,000 cm^{-1}, whose position depended on the nature of the solvent. Substance (VI) had a band at 23,200 cm^{-1}, whose position was constant in all solvents (table).

It was found that the relation between the position of ν_{max} of the absorption band and the dielectric constant was not linear. In the dielectric constant region of 5-27, this relation for (I), (III), and (V) was expressed by a bow-shaped curve, bulging toward the long-wave side, and for (IV) it was expressed by a curve bending in the other direction (Fig. 2). In the region of low dielectric constants (1.94-2.35), for (I), (III), (IV), and (V) the displacement of ν_{max} was quite large, but no regular relation between the changes in ν_{max} and the dielectric constant or the refractive index of the solvent could be detected. It is interesting that the curves expressing the relation between ν_{max} and the dielectric constant for aqueous dioxane solutions and for individual solvents did not conicide. This apparently indicates that the change in dielectric constant is not the only factor influencing the displacement of ν_{max} of solutions of cyclopentadienylides.

In an investigation of the absorption spectra of cyclopentadienylides (I, III, IV, and V) in acidified solutions it was found that in these cases, as in cases with pyridinium cyclopentadienylide (I) [2], the band at 18,000-21,000 cm^{-1} characteristic of cyclopentadienylides disappeared and a band appeared which probably corresponded to cation (VII), formed due to the addition of a proton of the acid to the negatively charged cyclopentadienylene residue of the bipolar ion.



(I) (VII)

Solvent	Dielectric constant	Position of maxima of main absorption band (ν in cm^{-1})				
		pyridinium cyclopentadienylide (III)	γ-benzylpyridinium N-cyclopentadienylide (III)	1-pyridinium 2,3,4,5-tetrabromocyclopentadienylide (IV)	2-methyl-5-vinylpyridinium cyclopentadienylide (V)	N-benzylpyridinium γ-cyclopentadienylide (VI)
Carbon tetrachloride	2,24[6]	18 400		19 400		
Benzene	2,25[6]	18 800	18 800	20 100	17 600	23 200
Toluene	2,35[6]	18 700		20 100		
Dioxane	2,24[6]	19 000	19 200	21 000	18 200	
Isooctane	1,94[7]	19 700		19 800		
Chloroform	5,1[8]	19 700	19 500	20 600	19 500	23 200
Pyridine	12,0[8]	19 400	19 300	21 700	19 500	
Acetone	21,0[6]	19 600	19 300	22 300	19 700	23 200
Ethanol	26,3[6]	20 000	19 800	21 600	20 000	23 200
Methanol	31,0[6]	20 600		22 000		23 300
Formamide	84,6	—		23 000		23 000—24 000
Acidified ethanol (10 ml of ethanol + 1 ml of conc. HCl)						
Dioxane– water		—		—		—
100%	2,24	19 000		21 000		
95%	4,0[9]	19 600		21 400		
90%	6,2[9]	20 000		21 800		
80%	12,2[9]	20 600		22 200		
70%	19,7[9]	21 200		22 600		
60%	28,1[9]	—		22 600		
50%	35,8[9]	—		22 800		

It is interesting to note that in solvents containing a labile hydrogen atom (methanol, ethanol, formamide) there are two absorption bands characteristic both of substance I and VII, indicating the simultaneous presence of the two substances in solution (Fig. 3).

In conclusion, we consider it our duty to thank I.V. Obreimov and D.N. Kursanov for interest in the work.

SUMMARY

1. We plotted the absorption spectra of γ-benzylpyridinium N-cyclopentadienylide (III), 1-pyridinium 2,3,4,5-tetrabromocyclopentadienylide (IV), 2-methyl-5-vinylpyridinium cyclopentadienylide (V), N-benzylpyridinium cyclopentadienylide (VI), and pyridinium cyclopentadienylide (I) in various solvents.

2. The spectra of cyclopentadienylides (III), (IV), and (V), like that of (I), have a characteristic absorption band in the region of 18,000-21,000 cm^{-1}, which is displaced with a change in the solvent.

3. N.Benzylpyridinium cyclopentadienylide (VI) has an absorption maximum in the region of 23,200 cm^{-1} in all solvents.

3. The magnitude of the dielectric constant of the solvent is not the only factor in determining the position of the maximum of the main absorption band.

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*Original Russian pagination. See C.B. translation.

ADDITION OF ETHYLENE CHLOROHYDRIN TO α-METHYLVINYL PHENYL ETHER

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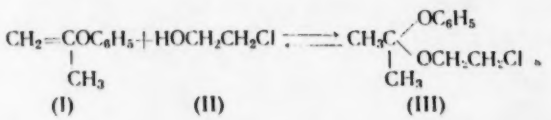
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 4, pp. 759-760, April, 1960
Original article submitted August 19, 1959

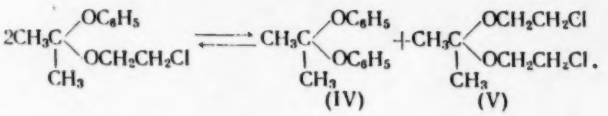
As previous investigations have shown-[1], the addition of ethylene chlorohydrin to vinyl alkyl ethers yields unsymmetrical β-chloroethyl alkyl acetals; when heated, the latter are symmetrized to form low-boiling dialkyl acetals and a high-boiling β,β'-dichlorodiethyl acetal. Unsymmetrical β-chloroethyl phenyl acetal behaves similarly [2].

The author decided to extend this reaction to α-alkylvinyl aryl ethers [3] and achieved it with α-methylvinyl phenyl ether (I) with ethylene chlorohydrin (II).



(I) (II) (III)

Due to the high tendency of the β-chloroethylene phenyl ketal of acetone (III) to symmetrize, it could not be isolated and we obtained only one of its symmetrization products, the diphenyl ketal of acetone (IV), and also one of the decomposition products, phenol.



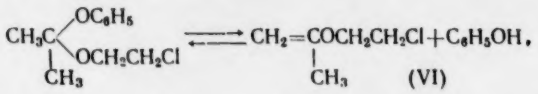
(IV) (V)

EXPERIMENTAL

To 10.0 g of ethylene chlorohydrin with b.p. 36-38° (6 mm); n_D^{20} 1.4410, in a three-necked, round-bottomed flask with a thermometer, reflux condenser, and dropping funnel was added an equivalent amount (16.8 g) of α-methylvinyl phenyl ether with b.p. 48-50° at 5 mm and n_D^{20} 1.5060. The α-methylvinyl phenyl ether was added to the ethylene chlorohydrin in the flask in 2 min and the temperature of the reaction mixture rose from 23 to 91°. The reaction mixture was stirred for a further hour, cooled, to room temperature, and vacuum distilled (26.2 g of product). We obtained the following fractions: I—with b.p. 77-84° (36 mm); n_D^{20} 1.4955; 7.5 g; II—with b.p. 73-92° (7-5 mm); n_D^{20} 1.4938; 5.0 g; III—with b.p. 97-100° (5 mm); n_D^{20} 1.4768; 3.0 g; residue in distillation flask 7.2 g. The losses were 3.5 g.

Fraction I (7.5 g) with b.p. 77-84° (36 mm); n_D^{20} 1.4955, consisted of a mixture, difficult to separate, of the β,β'-dichlorodiethyl ketal of acetone (V), α-methylvinyl β-chloroethyl ether (VI), and the phenyl β-chloroethyl ketal of acetone (III).

Fraction II (5.01 g) with b.p. 73-92° (7-5 mm) and n_D^{20} 1.4938 was a mixture of α-methylvinyl β-chloroethyl ether (VI) and the β-chloroethyl phenyl ketal of acetone (III).



Fraction III (3.0 g) with b.p. 97-100° (5 mm); n_D^{20} 1.4768 contained the β,β'-dichlorodiethyl ketal of acetone (V). From the residue (7.2 g) we isolated 3.0 g (22% of theoretical) of the diphenyl ketal of acetone (IV) with b.p. 130° (4 mm); n_D^{20} 1.5500; d_4^{20} 1.0705. Found: C 78.81; 78.78; H 7.25; 7.18%; MR 67.92; $C_{15}H_{16}O_2$. Calculated: C 78.92; H 7.07%; MR 67.55. The physical constants agree with literature data [4]. A small amount of phenol crystals were collected during the isolation of the diphenyl ketal of acetone.

SUMMARY

1. The reaction of α-methylvinyl phenyl ether with ethylene chlorohydrin was studied.

2. An indirect method was developed for the synthesis of the diphenyl ketal of acetone from α-methylvinyl phenyl ether and ethylene chlorohydrin.

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* Original Russian pagination. See C.B. translation.

RELATIVE REACTIVITY OF SOME ALKENYLSILANES IN THEIR INTERACTION WITH TRICHLOROSILANE

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The addition of hydrosilanes to vinyl- or allylchlorosilanes has been achieved previously either in the presence of peroxides [1, 2] or with a catalyst, namely, platinum on charcoal [3]. The use of these initiators required drastic experimental conditions, making it necessary to resort to reactions in autoclaves. In the present work we used Speier's catalyst (0.1 N solution of $H_2PtCl \cdot 6H_2O$ in isopropyl alcohol [4] for these additions and this made it possible to carry out the reactions under mild conditions at atmospheric pressure in a normal glass apparatus. Moreover, under our conditions the addition proceeded with heat evolution and cooling was required.

In order to determine the relative reactivity of allyl- and vinyltri-chlorosilanes in their reaction with trichlorosilane, we carried out a competing reaction, i.e., one equivalent of trichlorosilane was added to an equimolecular mixture of these alkenyltrichlorosilanes. As a result of this experiment it became clear that vinyltrichlorosilane is more reactive toward trichlorosilane than allyltrichlorosilane as 60.5% of it reacted, while only 40% of $Cl_3SiCH_2CH = CH_2$ reacted.

$$Cl_3SiCH=CH_2 + Cl_3SiCH_2CH=CH_2 + HSiCl_3 \longrightarrow 0{,}6Cl_3SiCH_2CH_2SiCl_3 + 0{,}4Cl_3SiCH_2CH_2CH_2SiCl_3 + 0{,}4Cl_3SiCH=CH_2 + 0{,}6Cl_3SiCH_2CH=CH_2.$$

By a similar competing reaction of $HSiCl_3$ with a mixture of $Cl_3SiCH = CH_2$ and $(C_2H_5)_2CH_3SiCH = CH_2$ it was possible to establish that the second compound is more reactive than the first; 77% of it reacted, while only 23% of $Cl_3SiCH = CH_2$ reacted. Finally, a comparison of the reactivity of $Cl_3SiCH_2CH = CH_2$ and $(CH_3)_3SiCH_2CH = CH_2$ in their reactions with $HSiCl_3$ showed that allyltrichlorosilane (60% reacted) is more active than allyltrimethylsilane (40% reacted)*. Thus, it became clear that the accumulation of negative chlorine radicals at the silicon atom promotes the addition of trichlorosilane to allylsilanes and inhibits its addition to vinylsilanes. The table gives the properties of compounds synthesized for the first time, including α,ω-disilylethanes, obtained by addition of hydrosilanes to various vinylsilanes and subsequent alkylation with RMgX or ArMgX.

EXPERIMENTAL

Vinyldibutylmethylsilane $CH_2 = CH(n\text{-}C_4H_9)_2SiCH_3$. To n-$C_4H_9MgBr$, obtained from 48.7 g of magnesium, and 300 g of n-C_4H_9Br in 0.7 liter of ether, was added 130 g of vinylmethyldichlorosilane [5]. After a day, the flask contents were boiled for 8 hr and then decomposed with 10% HCl. The ether layer and ether extracts from the aqueous layer were dried with $CaCl_2$. After removal of the ether, vacuum distillation of the liquid residue yielded 113 g of vinyldibutylmethylsilane with b.p. 85-86° (15 mm); the yield was 66.5%. The other vinylsilanes given in the table were synthesized analogously.

* The same conclusion was reached by Topchiev et al., [2], who added hydrosilanes to various allylsilanes in the presence of benzoyl peroxide, and by Petrov et al., [6], who used platinum on charcoal.

Sample No.	Compound	B.p. in °C (p in mm Hg)		n_D^{20}	d_4^{20}	MR		Yield in (%)
						found	calculated	
1	$(C_2H_5)_2CH_3SiCH=CH_2$	116,6	(750)	1,4225	0,7504	43,48	43,46	70
2	$(n\text{-}C_3H_7)_2CH_3SiCH=CH_2$	158	(742)	1,4330	0,7664	53,02	52,96	55,5
3	$(n\text{-}C_4H_9)_2CH_3SiCH=CH_2$	85	(15)	1,4390	0,7810	62,10	62,06	66,5
4	$(C_6H_5)_2CH_3SiCH=CH_2$	128,5—129	(1)	1,5716	0,9972	73,99	74,08	51
5	$(\alpha\text{-}C_{10}H_7)_2CH_3SiCH=CH_2$	238,5	(3)	m.p. 136,5—137,5°	—	—	—	22
6	$(C_6H_5)_2CH_3SiCH_2CH_2SiCH_3Cl_2$	171—173	(1,5)	1,5561	1,1134	98,02	97,33	85
7	$(C_6H_5)_2CH_3SiCH_2CH_2SiC_6H_5(CH_3)_2$	213,5—214,5	(1)	1,5740	1,0111	117,69	117,89	—
8	$(C_6H_5)_2CH_3SiCH_2CH_2SiCH_3(C_6H_5)_2$	290—292	(3)	m.p. 85—86°	—	—	—	50
9	$(\alpha\text{-}C_{10}H_7)_2CH_3SiCH_2CH_2SiCH_3Cl_2$	259—260	(2)	—	—	—	—	65
10	$(\alpha\text{-}C_{10}H_7)_2CH_3SiCH_2CH_2Si(CH_3)_3$	226	(1)	m.p.	—	—	—	60

Competing reactions. To a mixture of 29 g of vinyltrichlorosilane (0.18 mole) and 3.15 g of allyltrichlorosilane (0.18 mole) with 0.5 ml of Speier's catalyst was added 24.3 g of trichlorosilane (0.18 mole) with stirring. Heat was evolved during the reaction and therefore the rate of $HSiCl_3$ addition was such that the temperature did not rise above 100°. After being boiled for an hour, the contents of the flask were fractionated on a column. We recovered 11.5 g (0.0713 mole) of vinyltrichlorosilane and 19 g (0.108 mole) of allyltrichlorosilane, i.e., 60.5% of $Cl_3SCH=CH_2$ and 40% of $Cl_3SCH_2CH=CH_2$ reacted out of the amounts initially taken.

An analogous reaction with a mixture of 41.5 g of vinyltrichlorosilane (0.257 mole) and 33 g of diethylmethylvinylsilane (0.257 mole) and 35 g of trichlorosilane (0.257 M) with distillation of the product led to the recovery of 32 g of unreacted $Cl_3SCH=CH_2$ (0.198 mole) and 7.5 g of $(C_2H_5)_2CH_3SiCH=CH_2$ (0.0584 mole), i.e., 22.7% of $Cl_3SiCH=CH_2$ and 77% of $(C_2H_5)_2CH_3SiCH=CH_2$ reacted.

An analogous reaction with a mixture of 56.8 g of $Cl_3SiCH_2CH=CH_2$ and 37 g of $(CH_3)_3SiCH_2CH=CH_2$ with 44 of $HSiCl_3$ led to the reaction of 60% of the allyltrichlorosilane and 40% of the allyltrimethylsilane.

1-(Diphenylmethylsilyl)-2-(methyldichlorosilyl)-ethane $(C_6H_5)_2CH_3Si_3CH_2CH_2SiCl_2CH_3$. A small part (~5 ml) of a mixture of 47 g of diphenylmethylvinylsilane and 35 g of methylchlorosilane was placed in a flask and 0.5 ml of Speier's catalyst [4] added to it. A vigorous reaction was begun by gentle heating. The rest of the mixture was added at such a rate that the temperature in the flask did not rise above 100-120°. The flask contents were then heated at 150° for 2 hr. Vacuum distillation yielded 70 g of $(C_6H_5)_2CH_3SiCH_2CH_2SiCH_3Cl_2$ (85% yield).

SUMMARY

1. The relative reactivity of a number of alkenylsilanes in the addition of $HSiCl_3$ to them was estimated.
2. Ten organosilicon compounds that have not been described previously were synthesized.

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* Original Russian pagination. See C.B. translation.

LETTERS TO THE EDITOR

REVERSIBLE HYDRIDE TRANSFER AND ISOTOPIC HYDROGEN EXCHANGE BASED ON IT

Z.N. Parnes, M.E. Vol'pin, and D.N. Kursanov

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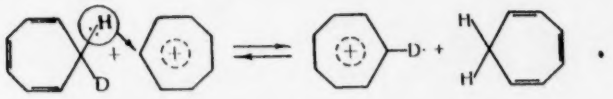
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 4, p. 763, April, 1960
Original article submitted January 3, 1960

Sir:

Many reactions in organic chemistry are often explained in terms of intramolecular or intermolecular or intermolecular hydride ions, i.e., by transfers of a proton and an electron pair in a single act, which are known as hydride transfers or transfers of hydride ions [1].

We have succeeded in demonstrating the existence of a reversible intermolecular hydride transfer. Such a transfer occurs between cycloheptatriene and a tropylium ion. In the reaction of deuterocycloheptatriene with tropylium bromide in formic and acetic acids, the deuterium which was initially in cycloheptatriene was redistributed completely between tropylium and cycloheptatriene as a result of equilibrium reactions of the type:



It was previously shown that a tropylium ion does not undergo hydrogen exchange with proton donors(deuterons) [2]. On the other hand, the transfer of a hydride ion as a kinetically independent particle is impossible in an acid medium.

Thus, the result we obtained can be explained only by a reversible hydride transfer occurring in the activated complex.

The ease of such a transfer of a proton and two electrons is evidently due to the advantage of forming a system of two electrons in the field of three nuclei in a transition state. We should also note that the reaction discovered is the first case in which reversible isotopic hydrogen exchange occurs as a result of the transfer of a hydride ion and not the migration of a proton (deuteron).

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*Original Russian pagination. See C.B. translation

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.–Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. – Publisher.

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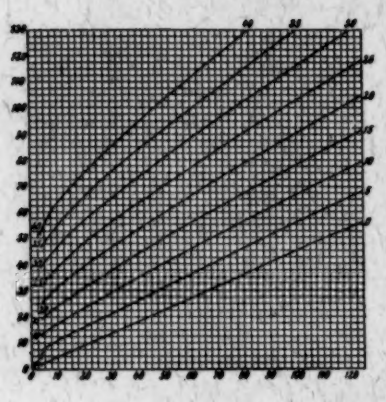

TABLES AND NOMOGRAMS OF HYDROCHEMICAL ANALYSIS

by I. Yu. Sokolov

Translated from Russian

Upon completion of analytical experiments, every research chemist, whether he uses a "test tube" or a "пробирка," must calculate his findings in the international language of figures in two forms (weights and equivalents), and often three (weights, equivalents and percent-equivalents), and then compare experimental data with theoretical values.

Technicians and statisticians working with the results of hydrochemical analyses performed at different times by different laboratories inevitably face the problem of converting their figures to one system.

All such calculations are considerably simplified by the use of the tables and nomograms in this book, originally published by the State Scientific and Technical Press for Literature on Geology and the Conservation of Mineral Resources, Moscow.

All the tables and nomograms are based on analytical results expressed in the form widely used in hydrogeological practice—milligrams per liter (weight form) and milligram-equivalents per liter (equivalent form). For calculation of percent-equivalents, the sum of cation equivalents and the sum of anion equivalents are taken as 100% each. Several new tables are presented for the first time, and the many tables for converting water-analysis results from one form to another make it possible to find the milligram-equivalents for any practically possible content of a component in water, accurate to the second decimal place, and the weight content of substances to tenths of a milligram.

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